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Synthesis And Stereochemistry Of Dimethylindium (iii) Derivatives

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SYNTHESIS AND STEREOCHEMISTRY OF DIMETHYLINDIUM(III) DERIVATIVES

by

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ABSTRACT

A number of new dimethylindium(III) derivatives have been synthesized in order to expand the field of organoindium chemistry and to determine the stereochemical properties of dimethylindium(III) compounds. The properties and structures are compared to analogous dimethylgallium(III) and dimethylthallium(III) compounds, and to some dimethyltin(IV) and trimethyltin(IV) derivatives.

Dimethylindium(III) chloride, bromide, and iodide are sublimable, dimeric, white crystalline solids. The low solubility and higher melting point relative to the other halides suggest that the fluoride may have a different structure, possibly being polymeric, similar to trimethyltin fluoride and dimethyltin difluoride.

Numerous Lewis base adducts of dimethylindium(III) chloride and iodide were studied. The ligands giving 1:1 adducts were pyridine, ammonia, triphenylphosphine (iodide only), triphenylphosphine oxide, and triphenylarsine oxide. These adducts are probably neutral, monomeric tetrahedral species. Ammonia also gave adducts in the ratio of 1:2 and 1:3 in the presence of excess ammonia, as studied by tensiometric titration. With the chloride, triphenylphosphine yielded a compound analyzed as bis[dimethylindium(III) chloride]-triphenylphosphine.

Other classes of dimethylindium(III) derivatives reported are those formed with anionic bidentate ligands (e.g. o-nitrophenoxide, acetylacetonate, and 8-hydroxyquinolinate); complexes of the chloride and iodide with neutral bidentate ligands (e.g. 1,10-phenanthroline, 2,2'-bipyridine, and ethylenediamine); and organoindium anions (e.g. tetraethylammonium and tetraphenylarsonium dimethylindium(III) dichloride, and lithium tetramethylindate). Various other derivatives including the hydroxide, 3,3,3-trifluoropropynyl, 1,1-bis(trifluoromethyl)ethoxide, and methoxide, and methylindium(III) dichloride and its pyridine and 2,2'-bipyridine derivatives, are discussed.

The most common stereochemistry for dimethylindium(III) derivatives is a tetrahedral arrangement about indium. Higher coordination, probably five, occurs in certain compounds, particularly the bidentate ligand complexes of the halides (e.g. dimethylindium(III) chloride-2,2'-bipyridine or -1,10-phenanthroline). In terms of chemical properties, dimethylindium(III) derivatives are generally more reactive towards decomposition (i.e. oxidation, hydrolysis, or thermal degradation) than known thallium analogues, being similar to dimethylgallium(III) compounds. The remarkable stability of a linear carbon-metal-carbon group as in the case of the dimethylthallium(III) moiety does not appear to be a significant property of the dimethylindium(III) species.

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INTRODUCTION

The growing interest in organometallic compounds in recent years has been further stimulated by the continuing discovery of novel properties - chemical, physical, and stereochemical - which these compounds possess. Five-coordination in triorganotin(IV) derivatives, polymerization by Ziegler catalysts, stabilization of unusual oxidation states, and electron deficient bonding in group II and group III organometallic derivatives are only a few of many examples. Among main group metals, organometallic derivatives of germanium, tin, and lead of group IV, aluminum of group III, beryllium and magnesium of group II, and lithium of group I have been extensively studied [1].

Trimethyltin(IV), dimethyltin(IV), trimethylantimony(V), and triphenyltin(IV) derivatives have been examined in this laboratory [2, 3] and interesting stereochemical problems have been encountered. These include polymeric, five-coordinate stereochemistry for trimethyltin fluoride [4, 5], perchlorate [6, 7], and tetrafluoroborate [8] and monomeric five-coordinate structures for trimethyltin bromide-ammine and -diammine [9]. These can be compared with the well known five-coordinate tin derivative, trimethyltin chloride-pyridine, studied by Hulme [10]

by X-ray crystallography. Similarly, trimethylantimony dichloride has a trigonal bipyramidal structure [11]. Organo-lead, -germanium, and -arsenic compounds apparently share this ability to form five-coordinate species, in addition to the already well-established four- and six-coordinate geometries.

In group III the situation is somewhat different. A great deal of investigation has been carried out on organoaluminum chemistry. Electron deficient bond arguments have been proposed to explain the bridging in certain compounds such as the trimethylaluminum dimer, thus increasing the coordination of aluminum from three for a monomer to four for a dimer. That aluminum prefers four-coordination is also shown by the formation of the chloride-bridged dimer of aluminum trichloride. Compared to the amount of study on aluminum chemistry, little has been accomplished in elucidating the properties of organometallic compounds of the heavier group III elements.

Various trialkyls of gallium have been synthesized. Coates and his colleagues have carried out a systematic study of trimethylgallium and certain dimethylgallium(III) derivatives [12, 13, 14]. It has been found that the organometallic derivatives of gallium closely resemble those of aluminum with respect to chemical reactivity.

Thallium trialkyls and dialkylthallium(III) derivatives have been isolated and studied since the beginning of this century, when Meyer and Bertheim [15] synthesized a number of dimethyl- and diethylthallium(III) derivatives. Shortly thereafter, Menzies [16, 17, 18] and Goddard [19, 20, 21] began their studies on dialkylthallium(III)

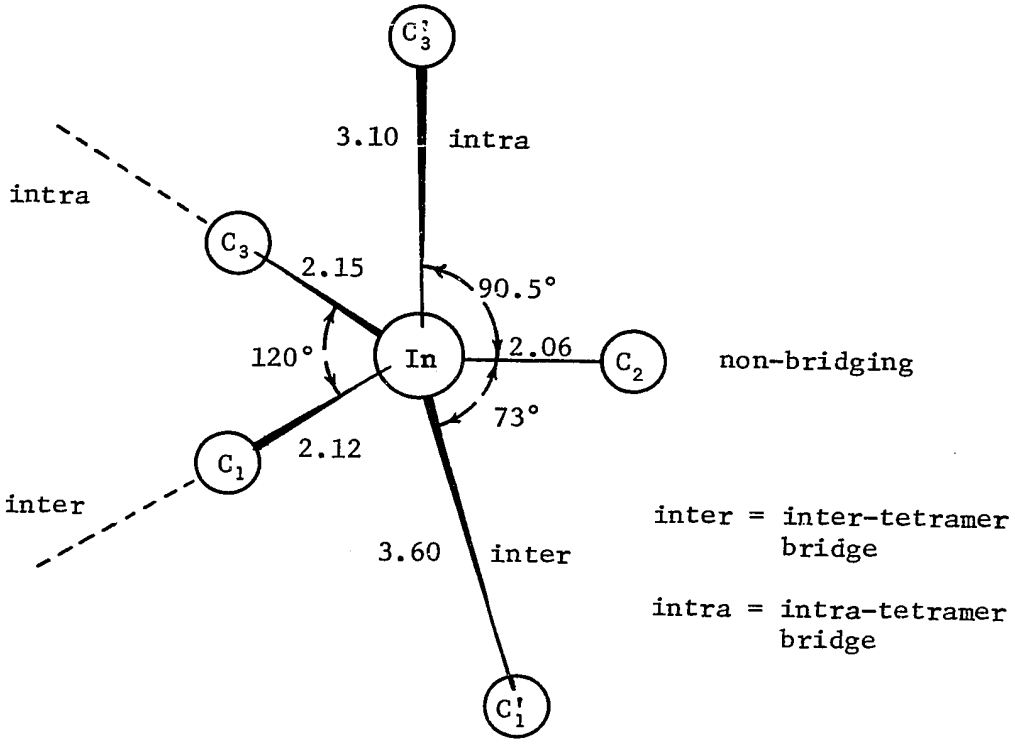
chelates and other derivatives. Most studies classify the dimethylthallium(III) derivatives of acids (e.g. dimethylthallium bromide [15], nitrate [19], and chromate [19]) as ionic salts. Thus these derivatives differ markedly from those of gallium and aluminum and also from organic derivatives of tin and lead, many of which have been regarded as covalent compounds.

By comparison, the organometallic chemistry of indium has received scant attention. Remarkably few papers have been published on the subject of organoindium compounds, many of the derivatives reported in the literature (see Appendix I) having been prepared incidentally during examinations of other group III compounds. Most of the previously reported organoindium derivatives have simply been prepared and not fully characterized.

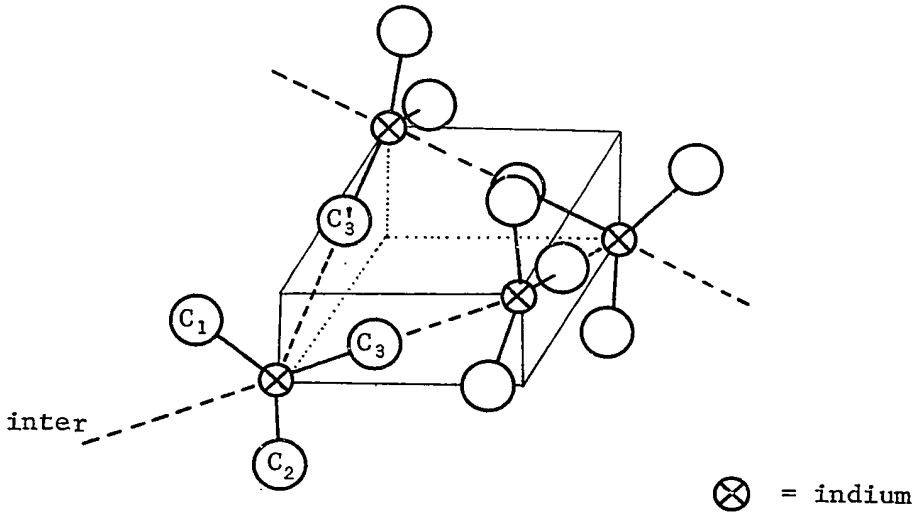
Trimethylindium [22], however, has been extensively studied and the stereochemistry has proved to be particularly interesting. In the crystal this compound is tetrameric, with bridging methyl groups giving distorted five-coordination about indium (see Figure 1) [23]. The bridging methyl groups are not equidistant from the metal atoms as is the case in the trimethylaluminum dimer. The trimethylindium moiety is nearly planar, with short indium-carbon bonds (2.06, 2.12, and 2.15 Å). One indium-carbon bond points almost directly normal to the trigonal plane of another trimethylindium species within the tetramer, the carbon being 3.10 Å from this second indium atom. A second indium-carbon bond in the original trimethylindium species points approximately at the trigonal plane of a trimethylindium molecule in an adjacent tetramer, this carbon-indium distance being 3.60 Å . The third methyl

Figure 1

Structure of Trimethylindium *



a) Configuration about indium



b) One trimethylindium 'tetramer'

* from reference 23.

group is non-bridging. Thus the trimethylindium tetramers are constructed of uneven methyl bridges, and are joined to neighbouring tetramers by different, unequal, methyl bridges. However this remarkable structure is broken down in benzene solution [24, 25] and in the vapour phase [26, 27], where trimethylindium is monomeric, having three-coordinate indium. Thus trimethylindium is somewhat different from the other group III trimethyl derivatives. Trimethylaluminum is a symmetrical methyl-bridged dimer, and the gallium and thallium analogues are monomers [1].

It appeared worthwhile to study the stereochemistry of diorganoindium(III) derivatives (and certain dimethylthallium(III) compounds) in an attempt to complete the comparison of stereochemistry and chemical properties of the organometallic derivatives of the group III metals. Further, comparisons between organic derivatives of group III and those of group IV, among others, could prove interesting. In particular, would these derivatives have unusual coordination as has been observed in some organotin compounds, and is the strong interaction (i.e. covalent bonding) of anions with organometallic derivatives of group IV (e.g. trimethyltin nitrate [6, 9] and perchlorate [6, 7]) also present in the group III analogues?

The first object, therefore, was to synthesize a series of diorganoindium(III) derivatives. There were several known species which could be used, dimethylindium(III), diphenylindium(III), and bis(pentafluorophenyl)indium(III) being three examples. Although the latter two species might prove more stable with respect to dissociation

or decomposition, the first, dimethylindium(III), was chosen on the grounds that it is the simplest. In addition, its derivatives are more likely to be soluble, hence easier to study by various techniques such as molecular weight, conductivity, nuclear magnetic resonance and solution phase infrared spectroscopy. In particular, infrared results would be simpler, and hopefully easier to interpret.

The symmetry of the dimethylmetal moiety has been considered by several workers, including Gutowsky [28, 29], Goggin and Woodward [30], and McGrady and Tobias [31, 32]. The infrared and Raman spectra of various species, such as dimethylthallium(III) [30, 33], dimethylcadmium [28], and dimethyltin(IV) [31], have been discussed. Basically the methyl-metal-methyl group may be linear or bent. In either case free rotation about the metal-carbon bond is expected. There are two skeletal stretching modes, the metal-carbon asymmetric and symmetric stretching vibrations.

According to Goggin and Woodward [30], Bauman [34] has shown that the appropriate effective point group for the linear structure is D_{3d}. In this structure the symmetric metal-carbon stretching vibration is infrared inactive, there being no change in the dipole moment of the molecule during this vibration. The mode is Raman active because the polarizability does change. Conversely, the asymmetric mode is infrared active but Raman inactive. In a bent structure, of symmetry C_{2v} [30], both stretching modes become Raman and infrared active.

A few examples of metal-carbon stretching frequencies are listed:

aqueous dimethyltin(IV) cation	530 cm^{-1}	31
dimethyltin dichloride-dipyridine	560 cm^{-1}	35
dimethylthallium perchlorate	557 cm^{-1}	33
dimethylcadmium	538 cm^{-1}	28

The presence of only one absorption attributed to a metal-carbon stretching vibration is interpreted as signifying a linear carbon-metal-carbon skeleton. Some other examples, with two metal-carbon stretching frequencies, are:

dimethyltin dichloride	563, 524 cm^{-1}	36
dimethylthallium acetylacetonate	552, 498 cm^{-1}	33
(dimethylphosphino)dimethylgallium	553, 518 cm^{-1}	14
dimethylindium dimethylphosphinate	528, 484 cm^{-1}	37

The two metal-carbon absorptions are attributed to a bent carbon-metal-carbon structure.

While the presence of two absorptions due to metal-carbon stretching vibrations suggests a bent structure, it really gives very little indication of the extent, or angle, of bending. However, the metal-carbon symmetric stretching absorption, usually the absorption of lower energy, is almost always significantly weaker than the asymmetric stretching absorption, usually being one half to one third as intense. Instances in which a very weak absorption has been assigned to the symmetric mode have been cited as examples of only slightly bent carbon-metal-carbon skeletons [38, 39]. In one case, dimethyl-

thallium perchlorate-1,10-phenanthroline, the suggestion of a nearly linear carbon-thallium-carbon group based on infrared evidence [38] has been upheld by the X-ray crystallographic study yielding a carbon-thallium-carbon angle of 168° [40].

Coates [1] has reviewed many of the known organoindium compounds. Therefore only a few of the reported derivatives will be discussed here, with reference to the analogous gallium or thallium derivatives. The trimethyl derivatives of all three metals are known, and are extremely sensitive to oxygen and water. Several dimethyl-metal derivatives are also known. The acetylacetonates appear to form a homologous series, being monomeric chelates with four-coordinate metal atoms. The methoxides are associated in solution, but the indium derivative is a liquid whereas the gallium and thallium derivatives are solids (melting points 24.5 - 24.7°C and 177 - 181°C, respectively). The cyanides of gallium and indium are tetrameric in benzene, but the thallium analogue is an ionic salt [41]. A principal difference is observed between dimethylgallium chloride, a volatile dimer which readily forms complexes with donor ligands, and dimethylthallium chloride, an ionic salt for which no addition complexes have been reported. An examination of Appendix I will show that many of the remaining dimethylindium(III) derivatives, for example the triphenylsiloxide, dimethylamino-, diphenylarsino-, and dimethylphosphinate, have a common property, namely, they are all dimeric or otherwise associated. Thus, by means of bridging, usually via oxygen or

nitrogen, the coordination of indium has been raised to four from three for an unassociated monomer. Thus all the dimethylindium(III) derivatives appear to have four-coordination about indium.

Coates [42] has remarked upon the high reactivity of one methyl group on trimethylindium towards an available hydrogen. Many of the reported dimethylindium(III) derivatives have been prepared from trimethylindium and the appropriate reagent such as methanol, methanethiol, and acetylacetone (enol form), by elimination of methane. Further, the methyl group from trimethylindium is sufficiently basic to extract a hydrogen atom from primary and secondary phosphines, arsines, and amines.

In studying the derivatives of dimethylindium(III) there are numerous compounds with which comparisons may be made. Not only the strict analogues, dimethyl-aluminum(III), -gallium(III), and -thallium(III), but also other types of organometallic moieties with a formal charge of plus one, including trimethyltin(IV), trimethylplatinum(IV), dimethylgold(III), and methyl-zinc(II), -cadmium(II), and -mercury(II) may be compared. While these have the same charge as dimethylindium(III), they may have differing coordination numbers and different degrees of filling of the electron orbitals (e.g. Au(III) is d^8, Hg(II) is d^{10}, and Pt(IV) is d^6, whereas In(III) could be considered to be d^{10}). Another type of comparison is with dimethylmetal species, regardless of charge. Dimethyl-beryllium, -zinc, -cadmium, and -mercury, and dimethyltin(IV) are examples. A third class, isoelectronic species, while useful in inorganic chemistry

(e.g. for comparing the isoelectronic ions Ag(I), Cd(II), In(III), and Sn(IV)), finds less applicability in organometallic chemistry. Two species isoelectronic with dimethylindium(III) are included in the above lists, dimethylcadmium and the dimethyltin(IV) cation.

The naming of compounds presented certain difficulties in some instances. Common usage often differs from, or is not covered by, the nomenclature approved by the International Union of Pure and Applied Chemistry [43]. For example, derivatives of 8-hydroxyquinoline have been identified by the following terms: 8-hydroxyquinolinato-, 8-hydroxyquinolinate, oxinate, and 8-quinolinolato-. The second name, being most common, will be used here. Moreover, certain formal names, such as di-μ-chloro-bis[dimethylindium(III)], are cumbersome and imply a specific structure to a compound in its normal state which may not be warranted on the basis of circumstantial evidence. Therefore a simpler name, in this case dimethylindium(III) chloride, will be used and signifies only a formula and implies nothing about structure or association. Similarly, addition compounds or complexes will be named in such a way as to identify the reagents rather than specifying the nature of the product, which may be uncertain.

Chapter 2

TRIMETHYLINDIUM AND DIMETHYLINDIUM(III) HALIDES

Trimethylindium had been the subject of extensive study by many researchers. Molecular weight determinations [22, 24, 25], electron [27] and X-ray [23] diffraction studies, Raman [44], infrared [45], and nuclear magnetic resonance [24] spectroscopic investigations, and vapour phase [26] and pyrolytic [46] studies have been carried out on trimethylindium. The compound has often been prepared from indium metal and dimethylmercury [22], other synthetic routes utilizing methylmagnesium chloride in ether [47], aluminum alkyls [48], or magnesium-indium alloy with methyl bromide [49]. Several of these preparations have disadvantages, including low yields, highly toxic reagents, length of reaction time, or interference from secondary products. Therefore the reaction of indium trichloride with methyllithium was investigated in the hope that it might prove to be a clean, simple preparative route.

The methyllithium reaction was a marked success in several respects. Upon mixing the reagents in ether, a vigorous reaction, with effervescence, ensues. When this ceases, within a quarter of an hour, all the volatile components, ether and trimethylindium, may be

removed *in vacuo* to a -196°C trap within three quarters of an hour. The yield is virtually quantitative, and is probably limited by the accuracy with which the methyllithium, in ether solution, can be measured. The reaction may be written:

$$3CH_3Li + InCl_3 \xrightarrow[ether]{} (CH_3)_3In + 3LiCl \qquad I$$

By changing the ratio of indium trichloride to methyllithium from 3:1 to 2:1, and shaking the ethereal mixture for one or two days, the product dimethylindium chloride may be isolated in 70 - 100% yield. However by fractionally distilling the reaction mixture immediately after the initial reaction ceases, trimethylindium in ether may be isolated. The residue contains lithium chloride and unreacted indium trichloride. Upon recombining the residue and the trimethylindium in ether and storing for two days, dimethylindium chloride is recovered in high yield. These results can be explained by the initial reaction of methyllithium yielding methylindium dichloride:

$$CH_3Li + InCl_3 \xrightarrow[ether]{} CH_3InCl_2 + LiCl \qquad II$$

This compound is much more soluble in ether (see chapter 7) than indium trichloride, hence it, rather than the trichloride, reacts with the methyllithium in solution, yielding dimethylindium chloride:

$$CH_3Li + CH_3InCl_2 \xrightarrow[ether]{} (CH_3)_2InCl + LiCl \qquad III$$

This product, also more soluble than the trichloride, interacts with methyllithium giving trimethylindium:

$$CH_3Li + (CH_3)_2InCl \xrightarrow[ether]{} (CH_3)_3In + LiCl \qquad IV$$

Equations II, III, and IV must be relatively fast reactions. Trimethylindium in the presence of indium trichloride must participate in an equilibrium reaction:

$$2(CH_3)_3In + InCl_3 \underset{ether}{\rightleftarrows} 3(CH_3)_2InCl \qquad V$$

which lies well to the right, yielding dimethylindium chloride as product. This is identical with the equilibrium of trimethylgallium and gallium trichloride [50], giving dimethylgallium chloride. Hence the overall reaction for II, III, IV, and V is:

$$2CH_3Li + InCl_3 \underset{ether}{\rightarrow} (CH_3)_2InCl + 2LiCl \qquad VI$$

It was found that adding one equivalent of lithium iodide to indium trichloride and two equivalents of methyllithium and shaking for two days in ether solution yielded dimethylindium iodide, uncontaminated by the chloride. In solution there are, formally, the species LiCl, LiI, and $(CH_3)_2InCl$. Undoubtedly halide exchange takes place in solution:

$$(CH_3)_2InCl + LiI \underset{ether}{\rightleftarrows} (CH_3)_2InI + LiCl \qquad VII$$

Hence $(CH_3)_2InI$ may be added to the list of species in solution. The order of solubility in ether is LiCl < LiI < $(CH_3)_2InCl$, $(CH_3)_2InI$. As ether is removed by evaporation *in vacuo*, lithium chloride precipitates, being the least soluble species. This will eliminate all chloride from the solution, leaving only dimethylindium iodide:

$$2CH_3Li + InCl_3 + LiI \underset{ether}{\rightarrow} (CH_3)_2InI + 3LiCl \qquad VIII$$

Both the chloride and the iodide were purified from the lithium halide by sublimation *in vacuo* at 110°C. Table 1 lists observations for

Table 1

Properties of Trimethylindium and Dimethylindium(III) Halides

$(CH_3)_2InX$ X	Molecular Weight calc. g.	found g.	conc. M x 10^2		Conductance Λ_m mho cm^2 $mole^{-1}$	conc. M x 10^3		Infrared In-CH_3 rock	ν In-C asym cm^{-1}	ν In-C sym
F	163.8							720 vs bd	548 s	493 m
Cl	180.3	385	0.82	b	3.4	2.32	a	732 vs bd	558 s	488 m
		413	1.01	b	4.1	5.99	a			
		427	0.53	b	3.0	1.90	f			
		227	4.06	a	69.2	1.31	c			
		221	2.67	a	61.5	2.10	c			
					53.0	4.27	c			
Br	224.7	513	1.07	b				735 vs bd	554 s	486 w
		502	0.80	b						
I	271.7	555	0.61	b	11.2	3.74	a	730 vs bd	548 s	(480 vw)
		<577	1.15	b	84.7	1.70	c			
CH_3	159.8	151±10	2.68	b	(ref. 25)			~700 vs bd	495 s (ref. 45)	
		178	0.4	† d	(ref. 24)					
		176±8	3	† e	(ref. 24)					
		178±3	3-24	† b	(ref. 24)					

a CH_3NO_2 d C_5H_{10} † concentration in mole %

b C_6H_6 e CH_2Cl_2

c CH_3OH f $C_6H_5NO_2$

s strong v very

m medium bd broad

w weak

several properties of these derivatives.

The remaining two halide derivatives were prepared by different methods. The bromide was isolated from the reaction of dimethylindium methoxide with hydrogen bromide in methanol. The fluoride was synthesized from trimethylindium and boron trifluoride, in ether:

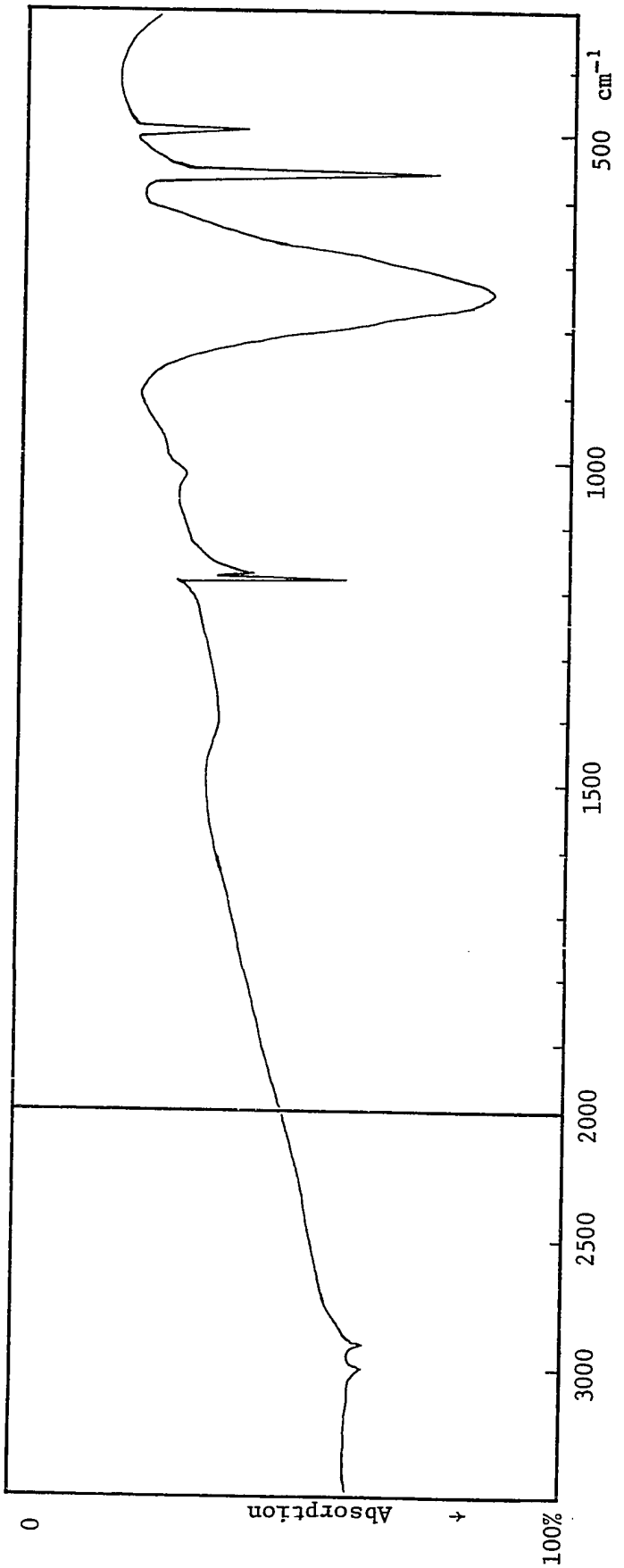
$$3(CH_3)_3In + BF_3 \xrightarrow[ether]{} 3(CH_3)_2InF\downarrow + [(CH_3)_3B\uparrow] \qquad IX$$

It formed a bulky white precipitate while the solution effervesced. Presumably trimethylboron (boiling point -21.8°C) was evolved. Both derivatives were purified by sublimation, the bromide at 110°C and the fluoride at 140°C (slowly) *in vacuo*.

The chloride, bromide, and iodide are fairly similar in their properties: melting points in the range 210 - 220°C; soluble in ether, methanol, and organic bases, slightly soluble in benzene and chloroform; air and moisture sensitive; dimeric in benzene; slightly ionized in nitromethane; and sublimable *in vacuo* at 110°C. The infrared spectra are very similar, having two indium-carbon stretching absorptions. Hence a bent C-In-C group is present in the structure. The infrared spectrum of dimethylindium chloride is shown in Figure 2. The peak assigned to the indium-carbon symmetric stretch in the iodide (Table 1) is very weak and its assignment is uncertain. In view of the dimeric nature in solution, and the low degree of ionization, these derivatives are probably dimeric in the solid state, with halogen bridges giving four-coordination about indium. Alternatively, a polymeric structure is possible, but is unlikely on the above evidence. Thus these derivatives are similar to dimethylgallium chloride, which is dimeric

Figure 2

Infrared Spectrum of Dimethylindium Chloride



in the vapour phase [50], and dimethylaluminum chloride, which is dimeric in both the vapour phase and solution [51].

Dimethylthallium chloride, bromide, and iodide are significantly different from the other group III analogues. According to an X-ray study [52] in 1934, these derivatives can be considered to be either aggregates of $(CH_3)_2Tl^+$ and X^- ions, or linear polymers with symmetrical halogen bridges. Each dimethylthallium(III) group, which is linear, is surrounded by four halide atoms in a plane through thallium, perpendicular to the C-Tl-C axis. Thus thallium has effectively six-coordination. The thallium derivatives are soluble only in basic media, such as pyridine or concentrated aqueous ammonia, from which they may be recrystallized. The iodide does sublime slowly at 150°C *in vacuo*. Thus there is a marked difference between the dimethylthallium halides and the gallium and indium analogues.

Dimethylindium fluoride differs from the other dimethylindium halides. It does not melt below 295°C; is soluble in pyridine, only slightly soluble in methanol, and is virtually insoluble in ether and chloroform; and sublimes slowly *in vacuo* at 140°C. These differences suggest that the fluoride may have a different structure from the other halide derivatives. Similar differences have been observed between trimethyltin fluoride and the other trimethyltin halides, and in this instance the fluoride is known [4, 5] to have a polymeric, fluoride-bridged structure whereas the other halides are tetrahedral monomers [53]. Similarly, dimethyltin difluoride has a fluoride-bridged stereochemistry, giving six-coordination to tin [54, 55].

Certain other monohalide organometallic compounds may be compared with the indium compounds. It is interesting to note that bis(pentafluorophenyl)thallium chloride and iodide [56] are dimeric in benzene solution. In acetone they have low conductances and are monomeric. Deacon and Nyholm suggest that these derivatives are dimeric in the solid state, with bridging halogens giving a tetrahedral array of ligands about thallium. Bis(pentafluorophenyl)indium bromide is also dimeric in benzene solution [57]. Thus these derivatives are structurally very similar to the dimethylindium halides.

Dimethylgold iodide is dimeric, with bridging halogens [58]. Trimethylplatinum chloride has a complex tetrameric structure in the solid state, with halogens bridging to give six-coordination about platinum [59]. Methylmercury halides have also been reported, and are monomeric with two-coordination about mercury [60, 61] although, as a result of molecular packing in the crystal, there is effectively octahedral coordination about mercury [62], analogous to the coordination about thallium in dimethylthallium halides.

It may be observed from these examples that halogen bridging is a common feature in organometallic derivatives in cases in which a (monomeric) compound would otherwise have a lower coordination number than is normal or stable. Thus dimethylindium halides, and analogous aluminum and gallium derivatives, achieve four-coordination about the metal atom by halogen-bridged dimerization. Very few three-coordinate indium derivatives are known, and these tend to be very reactive towards any species which will increase the coordination number to four.

Chapter 3

LEWIS BASE ADDUCTS OF DIMETHYLINDIUM(III) HALIDES

3.1 Simple 1:1 Adducts

Dimethylindium chloride and iodide form 1:1 complexes with many oxygen-, nitrogen-, and phosphorus-containing ligands. Tables 2 and 3 list the adducts prepared, and some properties.

The infrared spectra are generally very similar to a spectrum of the appropriate ligand superimposed on a spectrum consistent with a bent dimethylindium(III) species. Certain peaks may shift slightly upon complex formation. Spectra of the pyridine complexes of dimethylindium chloride and iodide have peaks characteristic of coordinated pyridine [35], particularly around 690, 630, and 430 cm^{-1}. Deacon and Nyholm have assigned many absorptions of certain coordinated ligands in organometallic complexes [63, 64]. In the infrared spectra of arylphosphine and -arsine ligands, certain modes , particularly ν P=O and ν As=O and, to a small extent, absorptions involving stretching or bending of the phosphorus-carbon or arsenic-carbon bonds coupled with aromatic ring vibrations (called X-sensitive modes), of the free ligands are shifted in the spectra of the coordinated ligands.

Table 2

Selected Properties of Lewis Base Adducts of

Dimethylindium(III) Halides

$(CH_3)_2InX$-L		Molecular Weight			Conductance	
X	L	calc. g.	found g.	conc. M x 10^2	Λ_m mho cm^2 $mole^{-1}$	conc. M x 10^3
Cl	NC_5H_5	259.4	316 b 272 a	2.32 4.50	6.4 55.2	2.43 a 3.44 d
Cl	$O=P(C_6H_5)_3$	458.6	467 b 521 b 435 a	1.13 2.74 2.89	7.9	1.59 a
Cl	$O=As(C_6H_5)_3$	502.5	560 b 574 b 533 a	1.41 2.74 5.31	13.4 13.6	2.47 a 1.96 a
I	$P(C_6H_5)_3$	534.0	459 b	3.43		
$[(CH_3)_2InCl]_2$-$P(C_6H_5)_3$		622.8	244 a 239 a	3.29 2.65	8.1 10.5 111.	0.70 a 0.62 e 1.57 d

a CH_3NO_2 d CH_3OH
b C_6H_6 e $C_6H_5NO_2$

Table 3

Selected Infrared Absorptions of Lewis Base Adducts

of Dimethylindium(III) Halides

$(CH_3)_2InX-L$		In-CH_3 rock	ν In-C asym	ν In-C sym
X	L		cm^{-1}	
Cl	NC_5H_5	720 vs bd	526 s	488 m
Cl	$O=P(C_6H_5)$	obscured	536 s 542*s	487 w 507*w 470*w
Cl	$O=As(C_6H_5)_3$	obscured	522 m	476*sh 469*s 462*sh
Cl	$x(OC_4H_8)$	720 vs bd	528 s bd	484 m
I	NC_5H_5	720 vs bd	522 s	482 m
I	$P(C_6H_5)_3$	724 s	515*s	478*m 495*s
$[(CH_3)_2InCl]_2-P(C_6H_5)_3$		730 s	544 m 515*s	498*s 492*s

s strong v very
m medium bd broad
w weak sh shoulder

* probably ligand absorptions

Appendix II gives a complete list of spectra of these dimethylindium-(III) derivatives, but a few peaks characteristic of coordinated ligands will be mentioned. The triphenylphosphine adducts have peaks at 1096 and 709 cm^{-1} (both X-sensitive modes). Coordinated triphenylarsine oxide has absorptions at 878 and 860 cm^{-1} (ν As=O) and triphenylphosphine oxide, at 1145 cm^{-1} (ν P=O). All of these compounds also have absorptions in the region 515 - 530 and 475 - 490 cm^{-1}, attributed to the indium-carbon asymmetric and symmetric stretching absorptions, respectively. In some cases ligand absorptions occur in the same region and make definite assignment of the peaks impossible.

The molecular weights of selected derivatives were determined in nitromethane or benzene solution (see Table 2). Dimethylindium chloride-pyridine, -triphenylphosphine oxide, and -triphenylarsine oxide appear to be slightly associated above 0.02 M in benzene solution, although the -triphenylphosphine oxide derivative approaches the formula weight upon dilution to 0.01 M. In nitromethane the observed molecular weights of these derivatives approximate to the respective formula weights. Dimethylindium chloride-pyridine and -triphenylphosphine oxide have very low conductances in nitromethane, suggesting very slight ionization of neutral species in solution. The chloride-triphenylarsine oxide complex, with a higher conductance, must be dissociated to a greater extent.

Therefore, on the basis of infrared data which support a bent C-In-C structure, molecular weight determinations which approximate to the formula weights, and conductances which indicate only very slightly

ionized neutral species, these derivatives are probably neutral, monomeric, tetrahedral molecules.

The triphenylphosphine oxide and the triphenylarsine oxide derivatives are soluble in chloroform and methanol, and tend to form viscous oils when recrystallization from one of these solvents is attempted. Good crystals were obtained by recrystallization from the ternary solvent system ether/chloroform/ petroleum ether. All of the 1:1 adducts described thus far are slightly soluble in ether. The pyridine adducts are also soluble in excess pyridine.

Dimethylindium iodide-triphenylphosphine oxide was prepared as a yellowish, sticky solid, and identified by comparison of its infrared spectrum with that of the chloride analogue. Silver iodide was instantly precipitated when a solution of silver nitrate in methanol was added to the iodide-triphenylphosphine oxide in methanol. Evaporation of the solution yielded a dirty gummy substance that was probably impure dimethylindium nitrate-triphenylphosphine oxide.

Dimethylindium iodide-triphenylphosphine, stored in a desiccator for several months, turned to a sticky, yellowish substance. Its infrared spectrum was identical to that of the gummy form of dimethylindium iodide-triphenylphosphine oxide, superimposed on a spectrum of the original iodide-triphenylphosphine. This finding, together with the observed decomposition of other 1:1 adducts over a period of time in dry air, support the conclusion (see Experimental Chapter) that dimethylindium(III) derivatives should be stored *in vacuo*, or at least under pure, dry nitrogen. Oxidation of triphenylphosphine derivatives

of bis(pentafluorophenyl)thallium halides has also been noted [64], yielding the triphenylphosphine oxide.

The dimethylindium halides are very soluble in certain basic, or coordinating, solvents, but can be recovered by removing the solvents *in vacuo*. Dimethylindium chloride absorbs tetrahydrofuran vapour exothermally, producing a liquid at 24°C. The infrared spectrum of this liquid shows significant differences in the 550 - 450 cm^{-1} region from that of dimethylindium chloride, and probably a complex, dimethylindium chloride-x(tetrahydrofuran), having a moderate dissociation pressure, is formed. Dimethylindium iodide is very soluble in acetonitrile, but this solvent may be removed readily *in vacuo*. Both dimethylindium chloride and iodide are very soluble in diethyl ether, and could be recrystallized from this solvent. Therefore, while coordination complexes are probably formed in solution, these are not readily isolable as stable solid or liquid compounds.

A number of 1:1 complexes of diethylaluminum halides with trimethylamine, pyridine, and tetrahydrofuran have been investigated [65]. These are monomeric in cyclohexane, and have low conductivity. Thus these results indicate a tetrahedrally coordinated aluminum atom. Diethylaluminum iodide-dipyridine was prepared, but its structure is uncertain [65].

Coates lists a few diorganogallium halide coordination complexes, including dimethylgallium chloride-trimethylamine and -trimethylphosphine [1].

Therefore the formation of 1:1 complexes of dimethylindium halides with Lewis bases is similar to the behaviour of analogous dialkyl halide derivatives of aluminum and gallium. Dimethylthallium halides, however, are very different in that they do not form addition compounds with monodentate ligands. In fact dimethylthallium chloride and iodide can be recrystallized from pyridine solution. Although thallium is generally a weaker acceptor atom, relative to aluminum, gallium, or indium, towards donor ligands, the failure of dimethylthallium halides to form complexes with Lewis bases may be due in part to a large crystal stabilization energy being realized in the ionic structure of the dimethylthallium halides [52].

Dimethylthallium perchlorate-pyridine has been discussed by Beattie and Cocking [38]. However this derivative should not be closely compared to the organoindium halide adducts because of the very different behaviour of halide ions (i.e. a strong tendency to coordinate as a ligand) compared to the perchlorate anion.

Deacon and Nyholm have commented upon a number of bis(pentafluorophenyl)thallium halide (chloride and bromide) complexes with triphenylphosphine, triphenylarsine, triphenylphosphine oxide, and triphenylarsine oxide [64]. These 1:1 adducts are monomeric in benzene and contain four-coordinate tetrahedral thallium. The fact that bis(pentafluorophenyl)thallium halides form 1:1 complexes with monodentate ligands, but dimethylthallium halides do not, is attributed [64] to the electronegative nature of the pentafluorophenyl group altering the energy separation between the 6s, 6p, and 6d orbitals on thallium.

Presumably, since a tetrahedral coordination is preferred, the energy separation between 6s and 6p levels must decrease, favouring tetrahedral sp^3 hybridization. The separation between 6p and 6d levels must increase, reducing the probability of forming more than four hybrid orbitals which would allow a higher coordination number, possibly five or six. In addition the bis(pentafluorophenyl)thallium halides, being soluble in polar organic solvents and apparently dimeric, apparently lack the high crystal energy of the dimethylthallium analogues. Thus the bis(pentafluorophenyl)thallium halides resemble the dimethylindium halides in forming 1:1 complexes with monodentate Lewis bases and, as will be described later, in also forming 1:1 complexes with bidentate ligands.

Lewis base adducts of other organometallic compounds are numerous. Beattie and McQuillan [35] list a series of organotin(IV) halide complexes, including trimethyltin chloride-pyridine and dimethyltin dichloride-dipyridine. The former has five-coordination [10] and the latter has six-coordination of the central tin atoms. In the dimethyltin(IV) derivatives, with octahedral coordination, the methyl groups are in a *trans* position, thus giving a linear C-Sn-C group. One example in the gold series, dimethylgold iodide-dibenzylsulphide [58], and in the platinum series, trimethylplatinum iodide-pyridine (dimer) [66], together with the preceding adducts, illustrate the wide occurrence of 1:1 adducts of Lewis bases with organometallic compounds. Conversely, alkylmercury(II) halides do not form complexes with donor ligands [1, 62] and are thus similar to the dimethylthallium halides. The same argument based on high crystal stabilization energy preventing adduct

formation may apply.

3.2 Ammonia Adducts

Ammonia forms a series of complexes with both dimethylindium chloride and iodide. These were identified by means of tensiometric titrations, and plots of results are given in Figure 3. Table 4 lists some properties of these complexes and Figures 4 and 5 give the infrared spectra.

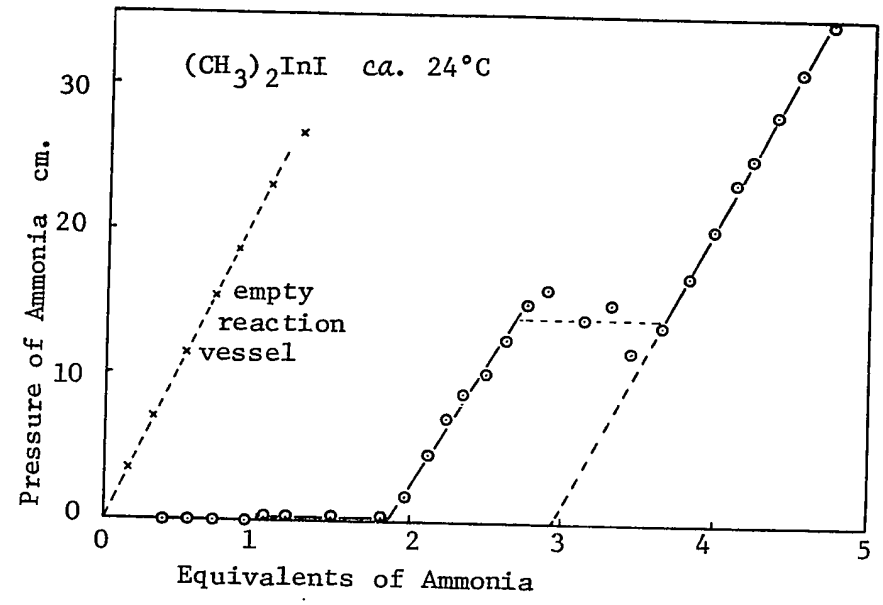
The chloride-ammine, iodide-ammine, and iodide-diammine are relatively stable with respect to dissociation under nitrogen. However, as can be inferred from the dissociation pressures, the chloride-diammine and both -triammines do dissociate under nitrogen, leading to difficulties in studying these derivatives. Mulls for infrared spectra and samples for melting point determinations of these complexes were prepared in an atmosphere of ammonia.

Results of further studies on these derivatives are of doubtful value because of the ready dissociation and disproportionation in solution. In addition all ammonia may be removed from the complexes by prolonged pumping *in vacuo*, leaving the original halides.

Therefore it is difficult to comment on the structures of these derivatives. Unfortunately infrared spectroscopy, which did give good spectra in many cases, is of little use at present because of the lack of spectra of ammonia, ammonium, and ammino- complexes of known structure with which to make comparisons.

Figure 3

Tensiometric Titration of Dimethylindium Chloride and Iodide with Ammonia



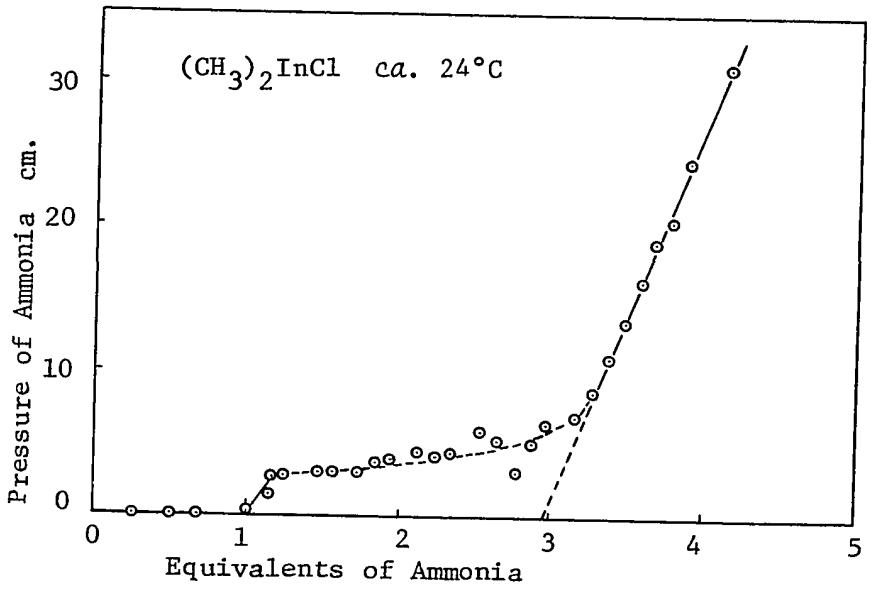


Table 4

Physical Properties of Ammonia Complexes of

Dimethylindium Chloride and Iodide

$(CH_3)_2InX\text{-}n(NH_3)$ X	n	"Melting* Point" °C	Dissociation Pressure at 24°C; cm	Comments
Cl	0.5	<20	0.05	sticky gum - probably dimethylindium chloride dissolved in the 1:1 adduct.
Cl	1	46-54	0.05	colourless crystals, soluble in ether.
Cl	2	37-55	2.7	white powder; infrared spectrum similar to that of 1:1 adduct.
Cl	3	42-73	3 - 5	bulky white powder; soluble in large excess of ammonia; dissociates under nitrogen.
I	1	<20	0.00	clear colourless liquid; soluble in ether.
I	2	87-115	0.1	white powder; scarcely soluble in ether or nitromethane; relatively stable under nitrogen.
I	3	100-119	12 - 15	bulky white powder; soluble in ammonia; readily dissociates under nitrogen.

* These derivatives appeared to soften and liquefy over a wide temperature range.

Figure 4

Infrared Spectra of Ammonia Complexes of Dimethylindium Chloride

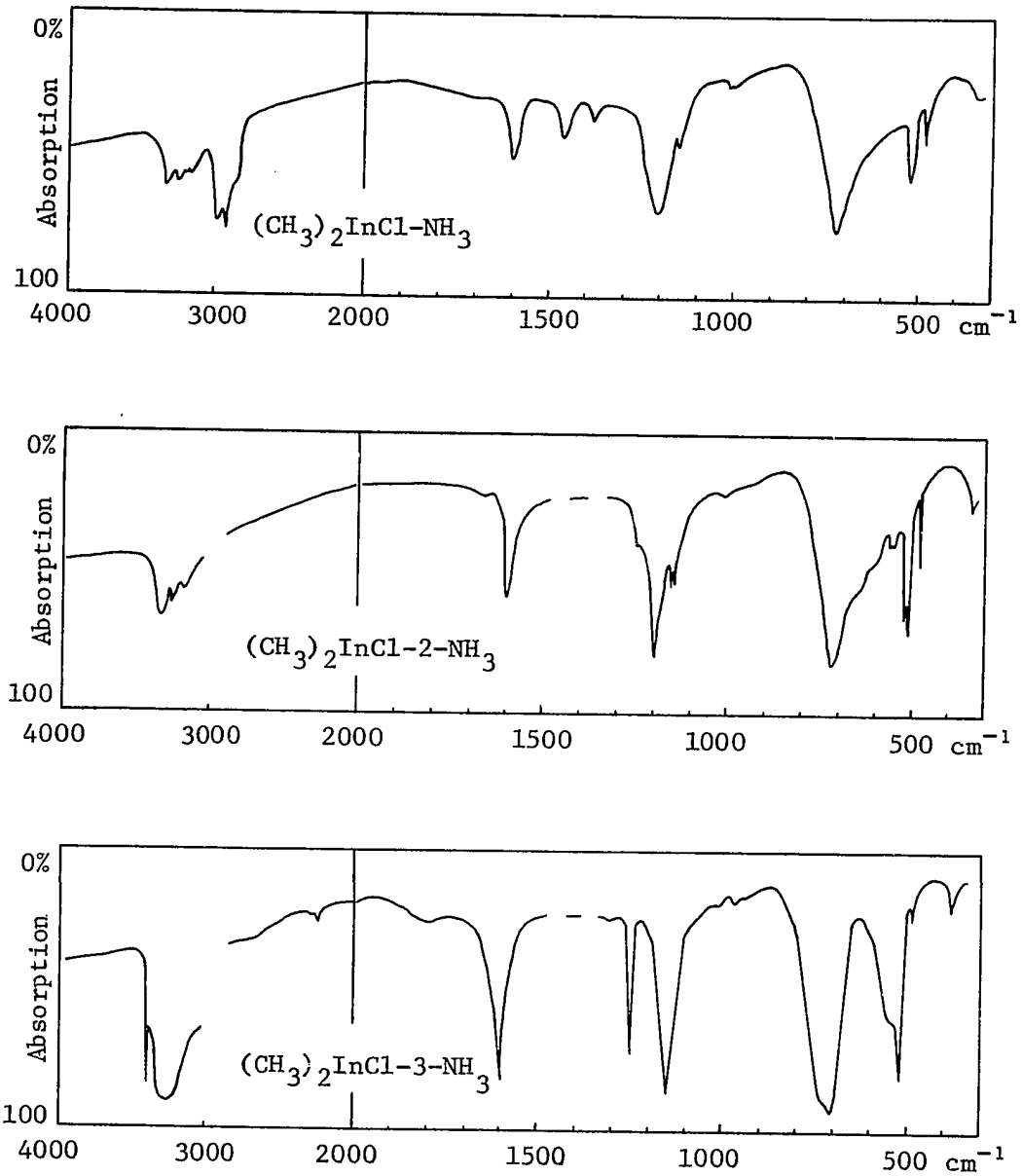
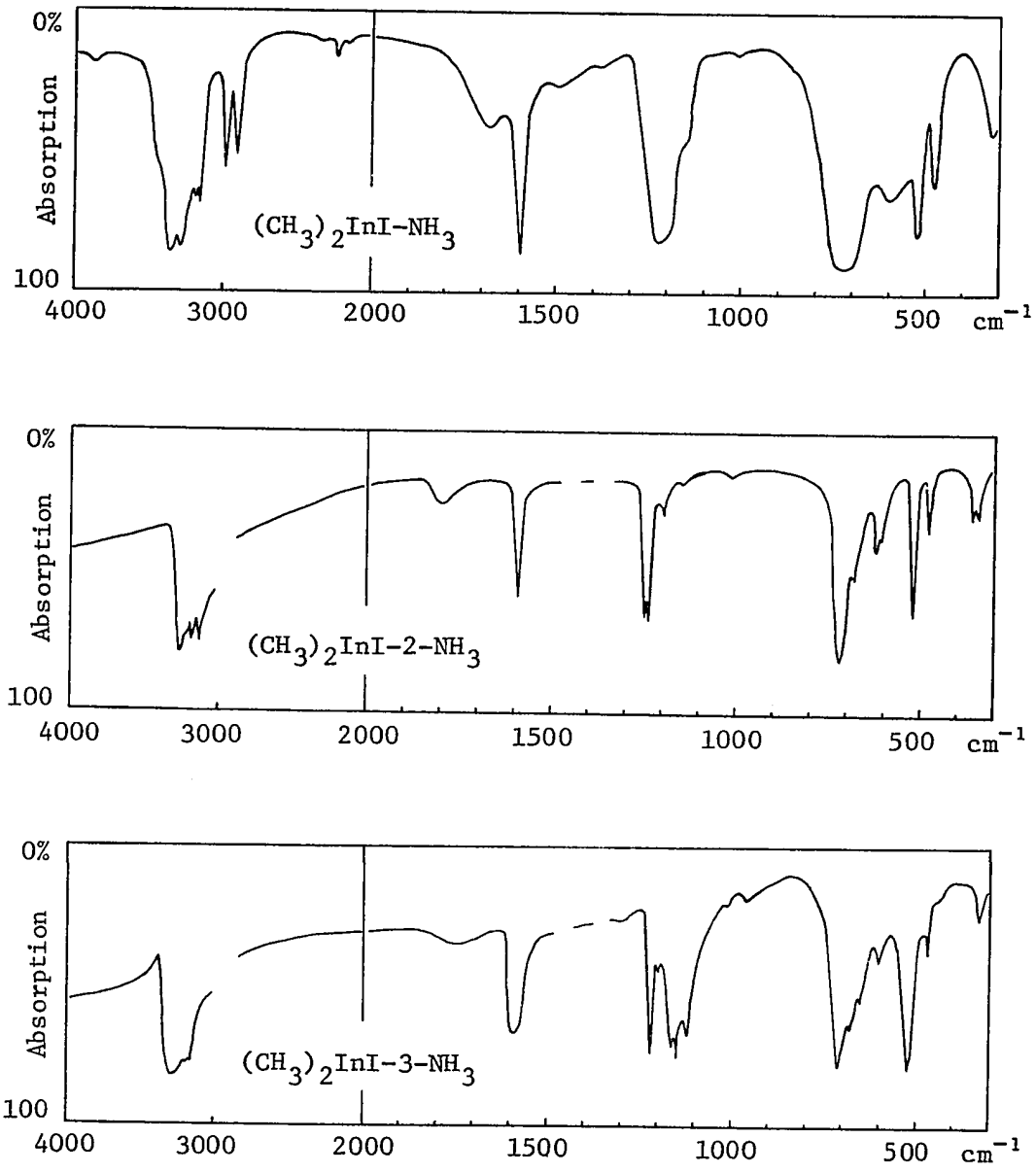


Figure 5

Infrared Spectra of Ammonia Complexes of Dimethylindium Iodide



Many peaks in the spectra may be assigned to coordinated ammonia by reference to published spectra of inorganic complexes [67] or organometallic derivatives [9, 68, 69, 70]. There are not, however, sufficient differences to unambiguously decide whether or not the ammino- group, NH_2, or the ammonium ion, NH_4^+, as well as coordinated ammonia are present.

In view of the melting points, the 1:1 complexes are probably neutral, tetrahedral species, similar to the 1:1 complexes discussed in the preceding section. The 1:2 complexes could have two coordinated ammonia molecules on each indium, leading to five-coordination about indium, or a salt-like structure, either $[(CH_3)_2In(NH_3)_2]^+ Cl^-$ or $[NH_4]^+ [(CH_3)_2InCl(NH_2)]^-$. The latter structure has been suggested for the gallium analogue [71]. Conversely Shriver and Parry [72] suggest that dimethylgallium chloride-diammine has the ionic formulation $[(CH_3)_2Ga(NH_3)_2]^+ Cl^-$. At room temperature the compound slowly decomposes to ammonium chloride and (ammino)dimethylgallium.

Considering the high dissociation pressures of the 1:3 complexes, the third molecule of ammonia is probably bound very loosely to the complex, and may be an ammonia of solvation rather than a ligand or actual chemical part of the complex. The infrared spectra do not support this explanation, because a complex spectrum of free and coordinated ammonia would then be expected. However the spectra are relatively simple.

Various other organometallic compounds give a series of complexes with ammonia. Diethylaluminum chloride-ammine (melting point

-11 to -10°C) and diethylaluminum chloride-diammine have been reported [73]. The latter complex is insoluble in hydrocarbons and ether, and may have the structure $[(C_2H_5)_2Al(NH_3)_2]^+ Cl^-$. Ethylaluminum dichloride forms a series of complexes with ammonia: 1:1, 1:2, 1:5, and 1:8 complexes being observed tensiometrically, and the first three having been investigated by X-ray powder photography.

Trimethyltin(IV) derivatives also form ammine complexes, trimethyltin bromide-ammine, $(CH_3)_3SnBr-NH_3$, and trimethyltin bromide-diammine, $[(CH_3)_3Sn(NH_3)_2]^+ Br^-$, being representative examples [9, 74]. Both probably contain five-coordinate tin.

Further afield, trimethylplatinum iodide-diammine is reported to have a six-coordinate structure [75]. Diethylgold bromide-ammine [76] is probably a neutral, square planar molecule.

It can be seen, therefore, that ammonia tends to form a wide variety of complexes, and the structures of only relatively few compounds have been satisfactorily established.

3.3 A 2:1 Adduct

With triphenylphosphine, dimethylindium chloride exhibits somewhat unusual behaviour compared to the formation of the 1:1 adducts already discussed. From an ether solution of dimethylindium chloride and triphenylphosphine a white, crystalline solid precipitates during concentration of the solution. The analytical results indicate that the composition is bis(dimethylindium chloride)-triphenylphosphine.

When the reactants are mixed in the ratio of 2:1, chloride to phosphine, in ether and the solvent is completely evaporated, the infrared spectrum of the product is identical to that of the previous precipitate. There are no indications in the spectrum of unreacted starting materials. The conductance in nitromethane is much too low for a 1:1 electrolyte, hence the structure $[(CH_3)_2In\text{-}P(C_6H_5)_3]^+ [(CH_3)_2InCl_2]^-$ is unlikely. The molar conductance does approximate to twice that of dimethylindium chloride, suggesting that in solution the only ionized species are those from dimethylindium chloride. The molecular weight determination in nitromethane, about 240 compared to 623 calculated for the 2:1 complex, indicates very little association of the two dimethylindium chloride molecules with the triphenylphosphine molecule in solution.

A similar phenomenon has been noted by Joshi and Wyatt [77]. Triethyltin chloride forms 2:1 complexes with dimethylamine, diethylamine, and trimethylamine (e.g. $[(C_2H_5)_3SnCl]_2\text{-}N(CH_3)_3$). On the basis of conductance measurements they suggest an ionic formulation, $[(C_2H_5)_3Sn\text{-}N(CH_3)_3]^+ [(C_2H_5)_3SnCl_2]^-$. They detected only a 1:1 adduct with pyridine, and no 2:1 complex.

Chapter 4

ANIONIC BIDENTATE LIGAND DERIVATIVES OF DIMETHYLINDIUM(III)

One of the few reported dimethylindium(III) derivatives is the acetylacetonate [42]. This derivative may be compared to the thallium analogue, dimethylthallium acetylacetonate, first synthesized in 1928 [78]. In a cursory X-ray study of the thallium derivative, Cox *et al.* [79] suggested that it has a tetrahedral distribution of valencies. They were unable to locate the positions of the methyl groups on thallium accurately. Many similar β-diketone derivatives of dialkylthallium(III) have been studied [18, 80, 81, 82], and all are considered to have bidentate chelate groups with four-coordination about thallium. Volatility, solubility in non-polar solvents, and a degree of association varying up to 1.7 in benzene solution have been observed for these compounds [80, 81].

More recently Okawara [39] has suggested that dimethylthallium acetylacetonate is weakly chelated in chloroform solution, and that in the solid state it has an ionic or weakly coordinated structure with a linear C-Tl-C moiety. These conclusions are based upon n.m.r. data and infrared spectra. Only one absorption in the 600 - 400 cm^{-1} region,

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at 552 cm^{-1}, was observed for the solid compound and was assigned to the thallium-carbon asymmetric stretch. Okawara used the absence of an infrared peak around 500 cm^{-1}, which could arise from the symmetric mode, to conclude that the C-Tl-C group is linear. The Raman spectrum of the solid does show a strong emission at 497 cm^{-1} but nothing around 550 cm^{-1}, supporting a linear stereochemistry.

On the contrary, a weak absorption in the infrared spectrum of solid dimethylthallium acetylacetonate has been observed in this research at 494 cm^{-1}, and in another laboratory [33] at 498 cm^{-1}. These observations support a bent C-Tl-C structure in the solid. In chloroform solution peaks are noted [39] at 566 (medium) and 482 (weak) cm^{-1}, indicating a bent C-Tl-C skeleton.

Dimethylindium acetylacetonate is very similar to the thallium compound in many respects (see Table 5). It sublimes *in vacuo* at 55°C; dissolves in ether, chloroform, and benzene; melts at 132 - 134°C (reported 118°C with decomposition [42]); and is slightly associated in benzene (observed molecular weight 302, 305, 297; calculated 243.9; degree of association 1.2). The infrared spectrum has three absorptions in the 560 - 460 cm^{-1} region; the 540 (strong) cm^{-1} peak is assigned to the acetylacetonate chelate ring [33], and the 550 (strong) and 486 (medium) cm^{-1} peaks to the indium-carbon asymmetric and symmetric stretching frequencies, respectively. This indicates that the C-In-C moiety is bent, and the molecule probably has a distorted tetrahedral arrangement about indium. The conductivity in methanol was found to be 26 mho $cm^2 mole^{-1}$, increasing with time. This behaviour suggests

that the compound is slowly solvolyzing. It was noted by Menzies *et al.* [78] that dimethylthallium acetylacetonate is ionized in aqueous solution. In nitromethane solution the conductivity of the indium derivative is essentially zero.

Coates and Hayter [12] have synthesized dimethylgallium acetylacetonate and noted that it is volatile and similar to the thallium compound. Thus the dimethylmetal acetylacetonates of gallium, indium, and thallium appear to be closely related structurally and form a homologous series.

Dimethylgold acetylacetonate [58] is thought to have a four-coordinated, square planar structure with a chelating acetylacetonate group. Miles, Glass, and Tobias have observed only a single gold-carbon stretching absorption, at 584 cm^{-1}, although a bent C-Au-C skeleton of a chelated four-coordinated gold should give rise to two absorptions. They suggest that the symmetric and asymmetric gold-carbon stretching modes are accidentally degenerate [32]. Trimethylplatinum acetylacetonate is a dimer [81] with six-coordination about platinum [83], but methylmercury(II) does not form a complex with acetylacetone [84]. In organotin chemistry, dimethyltin diacetylacetonate [85] has been shown to have octahedral coordination about tin, with a linear C-Sn-C group.

Thus, although the acetylacetonate group usually acts as a bidentate ligand, the actual structure of a complex depends upon a variety of factors, principally charge and electronic configuration about the metal. Group III elements appear to be satisfied with four-coordination, but transition metals have varying requirements, as

Table 5

Properties of Anionic Bidentate Ligand Derivatives of Dimethylindium(III)

$(CH_3)_2In(A)$ A	Molecular Weight calc. g.	found g.	conc. M x 10^2	Conductance Λ_m mho cm^2 $mole^{-1}$	conc. M x 10^3	Infrared In-CH_3 rock	ν In-C asym cm^{-1}	ν In-C sym
acetylacetonate	243.9	302	7.20 b	0	4.30 a	715 vs bd	550 s	486 m
		305	3.25 b	26.4 (incr.)	4.68 c		540*s	
		297	2.69 b					
o-nitrophenoxide	282.9	260	1.05 b			730 vs bd	550 s	497 w
		266	1.97 b				568*s	523*w
8-hydroxyquinolinate	289.0	564	0.26 b	0	<1.0 a	705 s bd	530 s	483 m
		593	0.25 b				572*m	498*m
							508*m	
[2-aminoethane sulphide]	221.0					700 s bd	505 m	
						720 sh bd	(460, 450, 430) s,bd	

a CH_3NO_2

b C_6H_6

c CH_3OH

s strong v very
m medium bd broad
w weak sh shoulder

* probably due to ligand

demonstrated above. Acetylacetonate derivatives of tin may also vary, some having six-coordination about tin. The compound dimethyltin chloride acetylacetonate, so far unreported, might be expected to have five-coordinate tin by comparison to the 8-hydroxyquinolinate derivative to be discussed shortly.

Dimethylindium o-nitrophenoxide was prepared as another example of a chelated organoindium derivative. It precipitates as bright orange crystals from ether, in which it is insoluble. This derivative is monomeric in benzene solution, and a chelated structure with four-coordinate indium is likely. Goddard [20] prepared the dimethylthallium analogue in 1921, and found it to be soluble in water, alcohol, acetone, pyridine, and chloroform. The infrared spectrum is difficult to assign because of o-nitrophenoxide absorptions in the 600 - 400 cm^{-1} region.

It was expected that dimethylindium 8-hydroxyquinolinate would be similar to the preceding compounds. It precipitates from ether as a bright yellow powder, and has negligible conductance in methanol or nitromethane. However the molecular weight in benzene is nearly that of the dimer (found 564, 593; calculated for dimer 578). Therefore this compound may have a dimeric structure with the 8-hydroxyquinolinate groups acting as bridging rather than chelating ligands. If this were true there are several possible structures, including interaction of the nitrogens with indium, forming a ten-membered ring, or bridging by the oxygens alone, giving a four-membered ring, In-O-In-O, as is suggested for dimeric dimethylgallium 2-dimethylaminoethoxide [12]. One property of the 8-hydroxyquinolinate and o-nitrophenoxide

derivatives that is worth noting is that they are air stable and do not decompose when exposed to air and light for many months. Most other dimethylindium(III) derivatives decompose within a few minutes to a few days when exposed. It is possible that the steric size of the ligands physically protects the species from oxidation or hydrolysis.

An attempt to prepare a fourth derivative of a slightly different nature was unsuccessful. Trimethylindium in ether was mixed with 2-aminoethanethiol, which is scarcely soluble, and a non-condensable gas, methane, was slowly evolved. The final product, a light orange-brown coloured powder, is insoluble in all common solvents, and involatile. Hence it could not be purified, and the analytical results (see Experimental Chapter) do not agree with the calculated values for dimethylindium 2-aminoethane sulphide.

Certain organometallic compounds that may be compared to these dimethylindium(III) derivatives will be discussed here and more fully in the next chapter. Dimethylthallium 8-hydroxyquinolinate has been reported [86] to have a chelated structure in chloroform, based on a study of the electronic spectrum. A chelated 8-hydroquinolinate derivative of [dimethyltin(IV) chloride]$^+$ has been reported [87] to have five-coordinate tin. This derivative should be compared to the dimethylindium 8-hydroxyquinolinate derivative because the dimethyltin(IV) chloride species is a singly charged cation, analogous to dimethylindium(III). However, the tin derivative has been found to be monomeric in benzene solution. Trimethyltin 8-hydroxyquinolinate

is also a monomer [87], with five-coordinate tin.

Dimethylzinc-bipyridine [88] is similar to the anionic bidentate ligand derivatives of dimethylindium(III) in that it has two methyl groups and a bidentate ligand on the central metal atom, giving a distorted tetrahedral stereochemistry similar to that expected for the dimethyl-gallium(III), -indium(III), and -thallium(III) derivatives discussed above.

Chapter 5

BIDENTATE LIGAND DERIVATIVES OF DIMETHYLINDIUM(III) HALIDES

Most of the dimethylindium(III) derivatives discussed thus far have tetrahedral coordination about indium. In an attempt to prepare organoindium derivatives with a higher coordination, either five or six, derivatives of the type $(CH_3)_2InX\text{-}(AA)$, where X is a halogen and AA is a bidentate ligand, 2,2'-bipyridine (bipyr), 1,10-phenanthroline (phen), or ethylenediamine (en), were synthesized. Table 6 summarizes molecular weight, conductivity, and infrared results for these compounds.

There are at least six simple structures possible for such derivatives (Figure 6): a) five-coordinate neutral monomer (I); b) tetrahedral ionic species with ionic halide (II); c) six-coordinate halogen-bridged dimer (III); d) mixed four- and six-coordinate ions, referred to as an ionic dimer [89] (IV); e) five-coordinate ligand-bridged dimer (V); and f) four-coordinate adduct with a monodentate ligand (VI). Structures I and IV might have isomeric forms.

Normal 1:1 electrolytes, such as tetraphenylarsonium chloride, have conductance values around 70 - 80 mho cm^2mole^{-1} in nitromethane. Hence dimethylindium chloride-phenanthroline, with a conductance of 6 mho cm^2mole^{-1} in nitromethane, must be a neutral species which

Table 6

Observations of Selected Properties of Dimethylindium Halide-Bidentate Ligand Derivatives

$(CH_3)_2In-(AA)$		Molecular Weight			Conductance			Infrared		
X	AA	calc. g.	found g.	conc. M x 10^2	Λ_m mho cm^2 $mole^{-1}$	conc. M x 10^3		In-CH_3 rock	ν In-C asym cm^{-1}	ν In-C sym
Cl	phen	360.5	366	1.85 a	6.2	0.95	a	obscured	522 s	483 m
			352	3.12 a	5.8	2.27	a			
Cl	bipyr	336.5	307	3.27 a	12.4	1.78	a	705 vs bd	529 s	481 m
			315	5.61 a	11.7	2.33	a			
			337	0.74 b	51.0	2.50	c		523 s†	481 m†
			350	1.39 b						
			407	2.17 b						
I	bipyr	427.9	418	2.31 a	28.2	1.09	a	obscured	539 s	480 vw
			431	0.97 b	25.3	1.74	a		525 s†	478 m†
Cl	en	240.4	295*	0.56 a	16.4	1.51	a	720 vs bd	515 s bd	481 m bd
I	en	331.8			90.7	1.35	c	722 vs bd	520 s bd	491 m bd

a CH_3NO_2
b C_6H_6
c CH_3OH

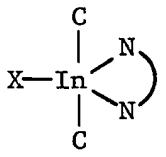
* validity in doubt
† chloroform solution

s strong bd broad
m medium v very
w weak

Figure 6

Possible Structures for Bidentate Ligand Derivatives

of Dimethylindium(III) Halides



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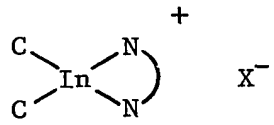
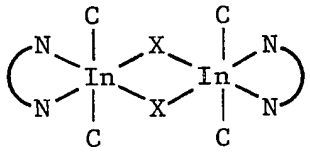
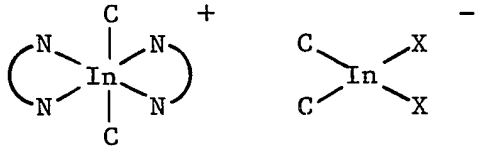


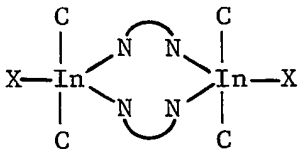
II



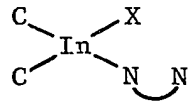
III



IV



V



VI

$\overset{\frown}{N\ N}$ = bidentate ligand

X = halide

C = methyl

ionizes to only a very slight extent. The molecular weights in both nitromethane and benzene are the same as the formula weights. At the low concentrations used in these studies, ion pair formation in a solvent of moderate dielectric constant such as nitromethane ($\varepsilon = 39$) is not expected to present a serious interference. Hence, of the possible structures I to VI, the neutral, five-coordinate structure I is most reasonable. Conductivity rules out ions such as II and IV; molecular weight eliminates III and V as the structure in solution; and the rigid stereochemistry of phenanthroline makes a bridging or unidentate interaction as in V or VI extremely unlikely [90].

Similarly the bipyridine derivatives of dimethylindium chloride and iodide are also expected to be five-coordinate monomers. In view of their shightly higher conductances they must be ionizing, perhaps to structure II, to a greater degree than the phenanthroline derivative. That the halide ion is ionizing is indicated by the fact that silver halide instantly precipitates when silver nitrate solution is added to the bipyridine or phenanthroline complexes in methanol. A series of molecular weight determinations of dimethylindium chloride-bipyridine in benzene solution indicates some association as the concentration is increased above 0.01 M, possibly due to dipole-dipole interaction [65]. It is reasonable, but by no means necessary, to suggest that this five-coordinate structure in solution is retained in the solid state.

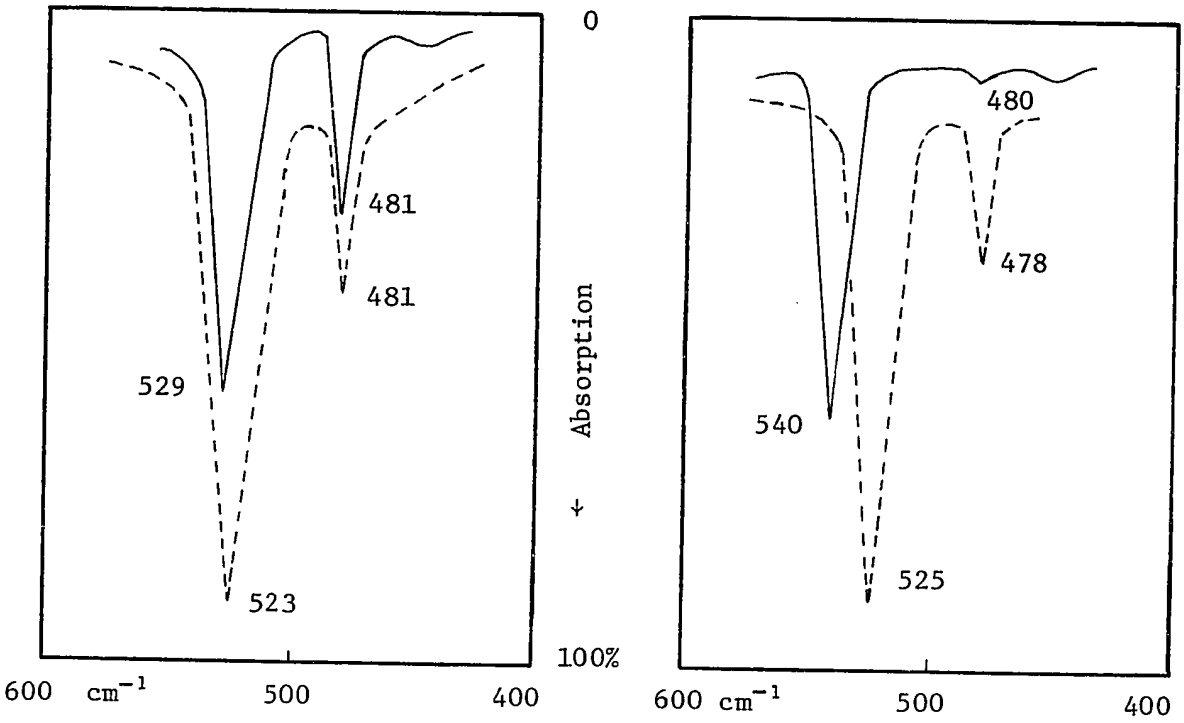
Unfortunately the infrared spectra are not of much assistance in determining the stereochemistry of these compounds. Certainly the

absorptions assigned to the ligands do agree with those reported for other compounds in which the ligands are bidentate [91]. In the case of dimethylindium chloride-bipyridine and -phenanthroline there are infrared absorptions around 525 (strong) and 480 (medium) cm^{-1} which can be assigned to the indium-carbon asymmetric and symmetric stretching frequencies, respectively. It can be inferred from the presence, and relative intensity, of the symmetric mode that the C-In-C moiety is definitely bent and not linear. However in dimethylindium iodide-bipyridine the symmetric stretching absorption is very weak, suggesting a more nearly linear C-In-C group in the crystal. In chloroform solution both the iodide and chloride bipyridine derivatives have symmetric stretching absorptions of medium intensity (see Figure 7), indicating that in solution the two derivatives are similar in structure. It is possible that crystal packing factors are effecting the structure in the solid state.

Assuming that these derivatives are five-coordinate about indium, there are certain comments regarding structure that may be made. For both bipyridine and phenanthroline, the angle N-In-N for a bidentate ligand will be less than 90° [56]. For example, in dimethylthallium perchlorate-phenanthroline this angle, N-Tl-N, is 63° [40]. Therefore a regular trigonal bipyramidal structure is not possible. In order to minimize the interaction between groups attached to indium, the bonds to halide and methyls should all be directed away from the bidentate ligand. A distorted tetrahedral arrangement of substituents on indium, with the bidentate ligand being considered as one substit-

Figure 7

Infrared Spectra of Bipyridine Derivatives of Dimethylindium Chloride and Iodide in the Indium-carbon Stretching Region



a) Dimethylindium chloride-bipyridine

b) Dimethylindium iodide-bipyridine

——— nujol mull

- - - - - chloroform solution

uent, may be a better spatial model than a distorted trigonal bipyramidal model. This would necessitate a bent C-In-C structure, as is indicated by the infrared spectra. As previously noted, dimethylindium iodide-bipyridine may have an essentially linear C-In-C group in the solid state. This could be a result of a halogen-bridged dimer (as in structure III) or a polymer which, upon dissolution, reverts to a five-coordinate species.

No strictly analogous compounds have been reported for gallium or thallium. Dimethylthallium iodide-phenanthroline has been synthesized, but studies of this derivative have been hindered by its low solubility in many solvents. It is soluble in pyridine. The closest analogue would be dimethylthallium perchlorate-phenanthroline [38, 40]. The X-ray structural determination of this compound has shown that, in the crystal, the effective coordination of six is best described as a distorted pentagonal bipyramid with one equatorial position vacant [40]. Perchlorate groups act as bidentate bridging groups with two oxygens coordinated to thallium and co-planar to the phenanthroline-thallium plane. The C-Tl-C group is slightly bent, with an angle of 168°, away from the phenanthroline. If the perchlorate groups interact strongly with the dimethylthallium(III) species (i.e. forming bonds), their symmetry should be reduced from T_d to C_{2v}. Significant changes in the infrared spectrum from that of the ionic perchlorate would then be expected [92]. However the infrared spectrum of the compound has a broad absorption at 1065 cm^{-1}, characteristic of the regular, tetrahedral perchlorate group. Hence the interaction between the perchlorate

uent, may be a better spatial model than a distorted trigonal bipyramidal model. This would necessitate a bent C-In-C structure, as is indicated by the infrared spectra. As previously noted, dimethylindium iodide-bipyridine may have an essentially linear C-In-C group in the solid state. This could be a result of a halogen-bridged dimer (as in structure III) or a polymer which, upon dissolution, reverts to a five-coordinate species.

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group and the dimethylthallium(III) cation is weak, and the thallium-oxygen distances are very long, 2.88 Å, compared to a calculated 2.62 Å for an ion-dipole contact [40].

Dimethylthallium perchlorate-bipyridine [33] has also been prepared, but no details were given. Some other bidentate ligand derivatives of organometallic compounds that have been reported are diphenylboron chloride-bipyridine, with the ionic formula [93] $[(C_6H_5)_2B(bipyr)]^+ Cl^-$, diphenylboron iodide-phenanthroline monohydrate, and bis(diphenylboron chloride)-bipyridine, $[(C_6H_5)_2B(bipyr)]^+ [(C_6H_5)_2BCl_2]^-$ [94]. Dimethylberyllium-, dimethylzinc-, and dimethylcadmium-bipyridine [88], while being derivatives of a neutral bidentate ligand, bear greater resemblance to the anionic bidentate ligand derivatives described in the previous chapter. The same comment applies to the derivatives bis(pentafluorophenyl)mercury-bipyridine [95] and -phenanthroline [96]. Dimethyl- and diphenyl-mercury do <u>not</u> form bipyridine derivatives. One rationalization is that mercury does not have sufficient electron accepting capacity to stabilize these derivatives [97]. Diethylgold bromide forms both 1:1 and 2:1 complexes with phenanthroline, $[(C_2H_5)_2Au(phen)]^+ Br^-$ and $[(C_2H_5)_2Au(phen)]^+ [(C_2H_5)_2AuBr_2]^-$ [90]. With bipyridine however, only the 2:1 complex is known. Brain and Gibson [58] suggest that this is due to the coordinating power of the halide ligand. Their argument is supported by the preparation of a 1:1 complex of the nitrate (which is generally a much weaker ligand than halide ions), $[(C_2H_5)_2Au(bipyr)]^+ NO_3^-$ [58]. Trimethylplatinum iodide-bipyridine has been reported [98] and is probably

an octahedrally coordinated complex.

Trimethyltin chloride does not form complexes with phenanthroline or bipyridine [35], although five-coordinate species such as trimethyltin chloride-pyridine [22] and trimethyltin fluoride [4, 5] are well known. The difference is that the trimethyltin(IV) group is planar with two *trans* substituents in the axial positions of a trigonal bipyramid. A bidentate ligand would of necessity have *cis* substitution and force the trimethyltin(IV) group out of planarity, as is observed for trimethyltin chloride, bromide, and iodide. However the dimethyltin(IV) moiety, isoelectronic with the dimethylindium(III) group, does form 1:1 complexes with both bipyridine and phenanthroline (e.g. dimethyltin dichloride-bipyridine [35]) having six-coordinate tin with a linear C-Sn-C group. Numerous such derivatives, $R_2SnX_2(AA)$ (where AA is a bidentate ligand), are known [99, 100] as well as others of the form $R_2Sn(AA^-)_2$, including dimethyltin di-8-hydroxyquinolinate [87, 99] and dimethyltin diacetylacetonate [85], all with a linear C-Sn-C skeleton and six-coordination about tin.

Five-coordination has been suggested for certain organotin(IV) derivatives, in particular dimethyltin chloride 8-hydroxyquinolinate [87] and trimethyltin 8-hydroxyquinolinate [101]. The former is analogous to dimethylindium chloride-bipyridine or -phenanthroline, with the exception that the bidentate ligand has, formally, a minus one charge. Two infrared infrared absorptions are assigned to tin-carbon stretching vibrations, the asymmetric and symmetric modes, suggesting that the C-Sn-C moiety is non-linear.

In resumé, dimethyltin(IV) species form six-coordinate compounds with neutral bidentate ligands, but the dimethyltin(IV) halide group forms a complex with an anionic bidentate ligand giving five-coordinate stereochemistry to tin; trimethyltin halides readily form derivatives with monodentate ligands, yielding five-coordinate tin, but not with common neutral bidentate ligands, although a five-coordinate 8-hydroxyquinolinate derivative of trimethyltin(IV) has been claimed. No six-coordinate trimethyltin(IV) species have been conclusively established, although Seyferth and Grim [102] have suggested an octahedral coordination about tin in the anion $[(CH_3)_3SnBr_2]^-$ because of halogen-bridged dimerization. They do state that $[R_3SnCl_3]^{2-}$ species are barely stable. This may explain the inability of trimethyltin chloride to form a complex with phenanthroline, for example.

As noted previously, the bis(pentafluorophenyl)thallium halides bear a striking resemblance to the dimethylindium halides in terms of stereochemistry. Deacon, Green, and Nyholm [56] have prepared the derivatives $(C_6F_5)_2TlX$-(phen or bipyr), where X is Cl^-, Br^-, NO_3^-, or $CF_3CO_2^-$. These are assigned a five-coordinate structure based upon conductivity and molecular weight data. "The bipyridine complexes are very weak electrolytes in acetone, and the molecular weights are slightly lower than the calculated values, confirming slight dissociation. The phenanthroline complexes are non-electrolytes and monomeric" [56]. In addition these compounds are monomeric in *ca.* 1% solution in benzene, but slightly associated in more concentrated solution. This general behaviour is remarkably parallel to that of the dimethylindium

halide-bidentate ligand derivatives just described.

A report by Cotton *et al.* [89] on compounds of the type TlX_3A_2 (where X is halogen and A is a Lewis base) indicates that the difficulty of making structural assignments based on conductivity results is not restricted to organometallic compounds. The derivative thallium trichloride-phenanthroline has a molar conductance of 52 mho cm^2mole^{-1} in acetonitrile, too low for a 1:1 electrolyte which is normally in the range 130 - 170 mho cm^2mole^{-1} in this solvent. If the ionic dimer formulation is used, $[Tl(phen)_2Cl_2]^+ [TlCl_4]^-$, the molar conductance becomes 104 mho cm^2mole^{-1} - still low for a 1:1 electrolyte. Hence the structure is uncertain, although Cotton favours the ionic dimer.

An interesting solvent-dependent reaction was observed in the preparation of dimethylindium chloride-bipyridine. This compound was readily prepared from ether solution. However when the reactants were mixed in methanol, white needle-like crystals slowly precipitated from solution. These were identified as methylindium dichloride-bipyridine. A rearrangement such as

$$2(CH_3)_2InCl \rightarrow CH_3InCl_2 + (CH_3)_3In \qquad I$$

is possible. In methanol solution the trimethylindium would immediately solvolyze to dimethylindium methoxide. However such a rearrangement seems unlikely because it has not been observed in many similar preparations of other compounds.

Rearrangement has been suggested [87] in the distillation of

trimethyltin 8-hydroxyquinolinate, which yields significant amounts of dimethyltin di-8-hydroxyquinolinate:

$$2(CH_3)_3Sn(Ox) \xrightarrow{\Delta} (CH_3)_2Sn(Ox)_2 + (CH_3)_4Sn \quad II$$

The ethylenediamine derivatives of dimethylindium iodide and chloride are more difficult to study. What appear to be non-stoichiometric solvates with a ratio of ligand to dimethylindium halide slightly exceeding 1:1 readily precipitate from ether solution. Recrystallization from methanol gives the 1:1 adduct in low yield, after removal of an unidentified, slightly soluble byproduct. It may be that rearrangement or decomposition is occurring in solution. Molecular weight studies give a weight slightly higher than the formula weight, suggesting slight association. However the conductance, while low, certainly signifies the presence of some ionized species. The validity of these results is open to question because of the low solubility of the 1:1 adducts and because of the suspected decomposition in solution. Therefore it is not possible to make any definite assignment of structure. Adequate analytical values for dimethylindium chloride-ethylenediamine were obtained only after very careful purification. Additional carbon, hydrogen, and chloride values for suspected solvates are given in the experimental section. Analytical results for the iodide-ethylenediamine derivative were less satisfactory.

Infrared spectra were again of little explicit assistance. It is noteworthy that the absorptions assigned to indium-carbon stretching

vibrations were not clean, sharp peaks but were broader than in most other dimethylindium(III) species. This could suggest that there is a randomness in the structure of these compounds, or that the methyl groups are not all in identical environments.

Only a few ethylenediamine complexes of other organometallic derivatives will be mentioned here. The compound dimethylthallium perchlorate-ethylenediamine has been reported [33] without comment. Ethylenediamine derivatives of dialkylgold halides have been the subject of some controversy. Burawoy and Gibson [103] originally suggested that compounds of the type $R_4Au_2Br_2$-en were neutral species with a bridging ethylenediamine group, $[R_2BrAu]$-en-$[AuR_2Br]$. Later Foss and Gibson [90] proposed the ionic dimer model, $[R_2Au(en)]^+$ $[R_2AuX_2]^-$, for such compounds as R = CH_3, C_2H_5, n-C_3H_7, and X = Br^-, I^-, or CN^-. 1:1 Adducts, for example dimethylgold iodide-ethylenediamine [32, 58], $[(CH_3)_2Au(en)]^+ I^-$, presumably with four-coordinate, square planar gold, have also been synthesized. Trimethylplatinum iodide forms two compounds with ethylenediamine, a 1:1 and a 2:3 complex [104].

The gallium analogue, dimethylgallium chloride-ethylenediamine, is thought to be ionic with four-coordinate gallium, $[(CH_3)_2Ga(en)]^+$ Cl^- [72]. This compound is briefly stable in water, and has a molecular weight equal to half the formula weight in this solvent, as would be expected for an ionic structure. Chloride may be replaced by sulphate by a metathetical reaction, and the infrared spectrum of the dimethylgallium(III)-ethylenediamine group is virtually unchanged by this

substitution.

Dimethylthallium halides do not form compounds with ethylenediamine, but may be recrystallized from this solvent.

Thus there appears to be little pattern or consistancy among the ethylenediamine derivatives of organometallic species. The observations for dimethylindium halide-ethylenediamine complexes do little to clarify either the trend in the group III analogues or the general situation.

Chapter 6

MISCELLANEOUS REACTIONS AND DERIVATIVES

Numerous reactions of diverse types were carried out in order to study the reactivity of trimethylindium and to prepare a range of dimethylindium(III) derivatives. The general purpose was to extend the field of organoindium derivatives and chemistry, and to seek out likely areas for more intensive study in the future.

In several instances the interest was not so much in the products as in the reactivity of trimethylindium. The reactions of this organoindium compound towards available hydrogen, even removing a proton from ordinary bases such as primary and secondary amines and phosphines, have been characterized by Coates [14, 42]. It has been found here that even an acetylenic hydrogen is 'acidic' enough to react with trimethylindium and eliminate methane. In other cases, the reactivity of trimethylindium is simply utilized as a convenient route to dimethylindium(III) derivatives.

Several other derivatives were prepared incidentally to the principal projects, or were byproducts in other reactions.

Table 7

Properties of Miscellaneous Derivatives

Compound	Molecular Weight				Conductance			Infrared		
	calc. g.	found g.	conc. M x 10^2		Λ_m mho cm^2 $mole^{-1}$	conc. M x 10^3		In-CH_3 rock	ν In-C asym cm^{-1}	ν In-C sym
$(CH_3)_2InOH$	161.8	508	1.03	b				700 vs bd	524 s	470 sh 465 sh ?
		306	0.95	b						
		305	0.69	b						
$[(C_2H_5)_4N]^+$ $[(CH_3)_2InCl_2]^-$	346.0	201	3.72	a	83.9	2.37	a	715 vs bd	512 s	483 m
		201	7.23	a						465 vw
$[(C_6H_5)_4As]^+$ $[(CH_3)_2InCl_2]^-$	599.0	341	5.75	a	71.0	2.25	a	obscured	512 m 511 m†	489 w 470*s
$(C_6H_5)_4AsCl$	418.8	202	5.95	a	73.3	3.82	a			
$(C_2H_5)_4NCl$	165.7	105	11.78	a	82.9	5.00	a			
		97.6 to 92.9	5.50	a						
$(CH_3)_2InOC(O)CH_3$	203.9				0	2.01	a	725 vs bd	548 s	490 m 455*s
$(CH_3)_2InOC(O)CF_3$	257.9	276	3.24	a	2.1	1.62	a	734 vs bd	564 s	518 m 497 w

a CH_3NO_2 c CH_3OH s strong w weak bd broad * probably ligand absorptions

b C_6H_6 m medium v very sh shoulder † chloroform solution

Table 8

Selected Infrared Absorptions of Some Miscellaneous Derivatives

Compound	In-CH_3 rock	ν In-C asym cm^{-1}	ν In-C sym
$(CH_3)_2In-C\equiv C-CF_3-(C_2H_5)_2O$	710 s bd	519 s	488 m
$(CH_3)_2In-O-C(CH_2)CH_3$ (acetone complex)	712 s bd	520 s 545*m	478 m 450*sh
$(CH_3)_2In-O-CH_3$	705 vs bd	517 s	470 s ? 495*s
CH_3InO	677 vs bd 720 sh ?		520 s 468 s ?
$Li^+[In(CH_3)_4]^-$	745 vs bd		430 vs bd
$(CH_3)_2In-O-C(CF_3)_2CH_3$	734 vs bd	540 vs	487 m 466*m 444*m

s strong v very

m medium bd broad

w weak sh shoulder

* probably ligand absorptions

6.1 Reactions of Trimethylindium with Compounds Containing Available Hydrogen

Trimethylindium reacted slowly with 3,3,3-trifluoropropyne in ether. Several products were obtained, two being unambiguously identified, one tentatively formulated, and the last being a sticky brown-black residue. Methane was evolved during the reaction, and this suggests that in the initial step trimethylindium reacted with the acetylenic proton:

$$(CH_3)_3In + H\text{-}C{\equiv}C\text{-}CF_3 \xrightarrow[\text{ether}]{} CH_4\uparrow + (CH_3)_2In\text{-}C{\equiv}C\text{-}CF_3\text{-ether} \quad \text{I}$$
$$\text{Ia}$$

Following fractional distillation of the solution, a colourless liquid was obtained in low yield. This decomposed slowly at -78°C in the dark, and fairly quickly at room temperature in the presence of light, giving a dark residue. The infrared spectrum of the liquid product has peaks in the indium-carbon stretching region (see Table 8) and rocking region, a strong peak at 2155 cm^{-1} attributed to C≡C stretching, several very strong peaks around 1200 cm^{-1} assigned to carbon-fluorine vibrations, and numerous other peaks. The proton n.m.r. spectrum shows a triplet and quartet assigned to ether, and a singlet at 10.2 τ, assigned to the protons of the indium methyl groups. Integration of the peaks showed a ratio of ethyl protons to indium methyl protons of 2.5 : 1. The calculated ratio for a 1 : 1 ether complex is 1.67 : 1. Some decomposition was noted in the n.m.r. tube, and may account for some loss of dimethylindium(III) from solution.

The colourless liquid was fairly stable with respect to

decomposition while in ether solution at 25°C. However, as an isolated product or in ether solution at 100°C, or in chloroform/trichlorofluoromethane solution, decomposition readily occurred. White crystals of dimethylindium fluoride precipitated from ether solution at 100°C, and a black-brown, fluorocarbon-containing tar formed:

$$(CH_3)_2In\text{-}C{\equiv}C\text{-}CF_3\text{-ether} \rightarrow (CH_3)_2InF\downarrow + \text{residues} \qquad \text{II}$$

In a recent review of organometallic acetylenes, Davidsohn and Henry [105] listed a number of dialkyl-aluminum and -gallium acetylenes. Some derivatives are thermally unstable, and all are sensitive to oxidation. Eisch [106] prepared the gallium derivatives from an acetylene and a trialkylgallium compound, eliminating one mole of alkane. Nast and Käb [107] have reported a series of dimethylthallium acetylenes, prepared in this instance from dimethylthallium-(III) derivatives, particularly (amino)dimethylthallium, and an acetylene in liquid ammonia. Therefore, while the product Ia has not been established directly, its identity as dimethyl(3,3,3-trifluoropropynyl)indium-etherate appears to be very reasonable.

Trimethylindium reacted with acetone in ether solution. Methane was evolved and a very unstable liquid product was recovered in low yield. This readily decomposed, producing a second substance, an inert insoluble white powder, as the principal product. This compound was identified as methylindium oxide by its infrared spectrum.

The infrared spectrum of the liquid product is complex and

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Trimethylindium reacted with acetone in ether solution. Methane was evolved and a very unstable liquid product was recovered in low yield. This readily decomposed, producing a second substance, an inert insoluble white powder, as the principal product. This compound was identified as methylindium oxide by its infrared spectrum.

The infrared spectrum of the liquid product is complex and

difficult to interpret (see Appendix II). The indium-methyl rocking mode is present, as are several peaks in the indium-carbon stretching region. Numerous absorptions in the 1750 - 750 cm^{-1} region could be attributed to ether and/or acetone. In the infrared spectrum of acetone, the carbonyl absorption is a broad peak at 1720 cm^{-1}. By comparison the liquid product has three absorptions in this region, at 1691, 1668, and 1618 cm^{-1}. Thus acetone is likely present and is either bonded to indium or coordinating in some manner, thus lowering the carbonyl stretching absorption. The reaction might be described as:

$$(CH_3)_3In + H_3C\text{-}C(O)CH_3 \rightarrow CH_4\uparrow + (CH_3)_2In\text{-}O\text{-}C(=CH_2)CH_3 \qquad \text{III}$$

This assumes that trimethylindium first reacts with the enol form of acetone as it does in the case with acetylacetone. The product then decomposes to the inert white powder, methylindium oxide.

Coates and Hayter [12] have reported that trimethylgallium forms a liquid 1:1 addition complex with acetone at room temperature. Between 50 to 90°C one mole of methane is evolved, leaving an involatile white product. This was assumed to be $(CH_3)_2Ga\text{-}OC_3H_5$. Further heating at 170°C liberated some more methane, and the solid turned orange-yellow. Thus trimethylindium appears to react with acetone, rather than simply forming an addition complex, more readily than trimethylgallium. The resulting product (assuming that the enolic hydrogen reacts in both cases), liquid $(CH_3)_2In\text{-}OC_3H_5$, then decomposes to methylindium oxide much more rapidly than the solid gallium analogue decomposes.

Trimethylindium reacts very vigorously with methanol, yielding the liquid, dimethylindium methoxide [42]. The reaction is less vigorous in ether solution. Coates has reported that the methoxide has a degree of association of about three in benzene. Dimethylgallium methoxide [12] is similar to the indium analogue, being dimeric. It melts at 24.5 - 24.7°C, and is relatively volatile, remaining dimeric in the vapour phase. Dimethylthallium methoxide [108] is somewhat different, being a crystalline solid with a high melting point, 177 - 181°C.

At -40°C trimethylindium reacts with water in ether, evolving one equivalent of methane and forming dimethylindium hydroxide. This compound, soluble in ether and slightly soluble in benzene, is a white solid that evolves methane *in vacuo*, decomposing to methylindium oxide in a few hours.

$$(CH_3)_3In + H_2O \xrightarrow[\text{ether}]{} CH_4\uparrow + (CH_3)_2InOH \qquad \text{IV}$$

$$(CH_3)_2InOH \downarrow \rightarrow CH_3InO + CH_4\uparrow \qquad \text{V}$$

Molecular weight determinations, even on freshly prepared samples, of the hydroxide were inconsistent and probably inaccurate because of decomposition, very low concentration, and incomplete dissolution of the sample. The compound does, however, appear to be associated (see Table 7).

Kenney and Laubengayer [109] have published a careful study of dimethylgallium hydroxide. It is trimeric in benzene solution, and although they claim it is fairly stable, it does decompose slowly in

air and rapidly at 150°C. In this case one equivalent of methane is liberated and a polymeric product, probably methylgallium oxide, is left. Dimethylthallium hydroxide is partially ionized in aqueous solution [110], and the compound is very stable [111]. There is therefore a marked change in character from dimethylgallium and dimethylindium hydroxides to dimethylthallium hydroxide. Principally, the stability of the dimethylthallium(III) species is much greater with respect to decomposition, hydrolysis, or oxidation than that of dimethylgallium-(III) or dimethylindium(III).

The preparation of bis(dimethylindium)oxide was attempted:

$$2(CH_3)_3In + H_2O \not\rightarrow [(CH_3)_2In]_2O + 2CH_4 \qquad VI$$

but was apparently unsuccessful. Methylindium oxide precipitates, and some trimethylindium is left unreacted.

6.2 Dimethylindium(III) 'Salts'

The preparation of several dimethylindium(III) 'salts' was attempted, with varying degrees of success. Two derivatives, dimethylindium acetate and trifluoroacetate, were easily synthesized from trimethylindium and the respective acetic acid, in ether solution. Both are sublimable, white crystalline solids, non-conducting in nitromethane. The trifluoroacetate is monomeric in this solvent, and soluble in warm ether. The carboxyl absorption in the infrared spectrum of the trifluoroacetate is at 1620 cm^{-1}, as compared with 1780 cm^{-1} for trifluoroacetic acid, suggesting strong interaction of the carboxyl group with the organometallic cation. Thus it is

possible that the trifluoroacetate group is acting as a monodentate or bidentate ligand, or a bridging group in the solid state, in this compound. An analogous compound, bis(pentafluorophenyl)thallium trifluoroacetate [56], has a very similar spectrum (e.g. ν $-CO_2-$ asym. is at 1608 cm^{-1}) and here also the structure is uncertain.

Dimethylindium acetate is much less soluble and more difficult to sublime that the trifluoroacetate derivative. The infrared spectrum is fairly similar to the spectrum of bis(pentafluorophenyl)thallium acetate or dimethylthallium acetate [56]. Deacon and Nyholm suggest that the dimethylthallium derivative may be ionic, but that the bis-(pentafluorophenyl)thallium acetate may be dimeric with bridging acetate groups.

Coates has reported that dimethylgallium acetate is dimeric in acetone [12], but it is not possible to distinguish between a single bridging oxygen (hence a four-membered ring, Ga-O-Ga-O) and both oxygens on each acetate group bridging (an eight-membered ring). The structure of dimethylthallium acetate, which completes the acetate series, is uncertain and will be discussed more thoroughly in section 6.5.

Trimethyltin acetate has recently been shown to exist in two forms, an insoluble, polymeric form and a soluble, cyclic form, both with bridging acetate groups [112].

Silver halide is precipitated when a solution of a silver salt is added to a solution of a dimethylindium halide in methanol. Thus,

what may be crude forms of dimethylindium nitrate, tetrafluoroborate, and perchlorate may have been prepared. There were certain complications which interferred in some of these preparations. Sometimes a black deposit results just after silver halide precipitates. This was avoided in the case of the tetrafluoroborate by using dilute methanolic solutions, and adding the silver tetrafluoroborate solution slowly in order to keep the concentration of silver ions in solution as low as possible. Upon evaporation of the solutions amorphous grey solids resulted. The perchlorate derivative exploded upon scraping with a spatula.

This field of organoindium 'salts' has thus been scarcely touched. It is certainly worth extensive study, although various synthetic routes may have to be utilized in order to prepare some of the compounds.

6.3 Complex Organoindium Anions

Two organoindium anions have been synthesized. The lithium salt of the tetramethylindate anion, $Li^+ [In(CH_3)_4]^-$, results from mixing trimethylindium and methyllithium in ether solution. The product, consisting of involatile white crystals, is highly sensitive to oxidation and hydrolysis, soluble in ether, and just slightly soluble in chloroform. Thus in the original preparation of trimethylindium an excess of methyllithium above three equivalents relative to indium trichloride must be avoided to prevent formation of lithium tetramethylindate.

Various group III analogues have been reported. Williams and Brown [113] have studied alkyl group exchange of lithium tetramethylborate, lithium tetramethylaluminate [114], and lithium tetraethylgallate by nuclear magnetic resonance spectroscopy. These derivatives are very similar in chemical properties - extremely sensitive to oxidation and hydrolysis, soluble in ether, and slightly soluble in benzene.

The second anion, [dimethylindium dichloride]$^-$, was prepared as the salt of the tetraethylammonium and tetraphenylarsonium cations. Both compounds are dissociated in nitromethane (see Table 7), although under these conditions slight ion pair formation may account for the observed molecular weights not being exactly half the formula weights as required for complete ionization. Also, both derivatives are highly conducting in nitromethane, suggesting that they are 1:1 electrolytes. These derivatives, which are white crystalline solids, are very soluble in methanol and chloroform but insoluble in ether. The tetraethylammonium derivative does, however, become a sticky, white viscous liquid in warm ether. The indium atom in the anion is undoubtedly tetrahedrally coordinated by the two methyl groups and the two halide atoms.

Such anion formation of organometallic halides with halide ions is well known. Various organothallium derivatives have been reported: $[(CH_3)_4N]^+ [C_6H_5TlCl_3]^-$ and $[(CH_3)_4N]^+_2[C_6H_5TlCl_4]$= [115]; and $[Q]^+ [(C_6F_5)_2TlX_2]^-$ (where Q is tetraphenylphosphonium or tetraethylammonium, and X is chloride or bromide) [56]. These latter derivatives

are 1:1 electrolytes, with four-coordination about thallium.

An organogold anion, $[(C_2H_5)_2AuBr_2]^-$, has already been described [90]. Numerous organotin anions have also been studied, including $[(CH_3)_2SnCl_4]^{2-}$ [102], $[(CH_3)_3SnBr_2]^-$ [102], $[C_2H_5SnCl_4]^-$, $[(C_2H_5)_2SnCl_3]^-$ [116], $[(CH_3)_2SnCl_3]^-$ [100], and $[(C_6H_5)_3SnCl_3]^{2-}$ [117].

6.4 An Insertion Reaction

The reaction of trimethylindium with hexafluoroacetone appears to be novel and unique in this study. The product is a viscous, scarcely volatile liquid which apparently oxidizes or hydrolyzes readily. Proton magnetic resonance shows two signals, in the ratio of 2:1, at 9.91 and 8.48 τ. The stronger peak is at high field where signals due to protons of dimethylindium(III) occur (see Appendix III). The infrared spectrum has peaks characteristic of the $-CF_3$ group in the 1250 - 1050 cm^{-1} region, C-H absorptions at 3000 and 2930 cm^{-1}, a broad peak at 734 cm^{-1} attributed to indium-methyl rocking, and several peaks in the 540 - 440 cm^{-1} region, two of which could be assigned to indium-carbon stretching modes. There is no strong absorption in the 2000 - 1500 cm^{-1} region where a carbonyl group normally absorbs. Analytical results are close to values calculated for a 1:1 complex of trimethylindium to hexafluoroacetone, and the slight deviation could readily be due to decomposition. Thus on the basis of this evidence the reaction is thought to be an insertion of the carbonyl group into an indium-carbon bond:

$$(CH_3)_3In + O{=}C(CF_3)_2 \xrightarrow[\text{ether}]{} (CH_3)_2In\text{-}O\text{-}C(CF_3)_2CH_3 \qquad VII$$

The product then is dimethylindium 1,1-bis(trifluoromethyl)ethoxide.

Although this type of reaction may be uncommon for trialkylindium compounds, it has been observed in numerous reactions involving hexafluoroacetone. Janzen [118] has investigated the insertion of hexafluoroacetone into the silicon-hydrogen bond in a number of alkylsilanes. The products all contain a silicon-oxygen bond, not a silicon-carbon (of the hexafluoroacetone moiety) bond. In another reaction, hexafluoroacetone is inserted into a hydrogen-oxygen bond in water, yielding hexafluoropropane-2,2-diol.

Thus the reaction with trimethylindium is not unreasonable, and the proposed structure, with indium bonded to oxygen, is analogous to the other reactions of hexafluoroacetone.

At least two mechanisms could readily be used to explain this reaction. In an ionic mechanism [118], trimethylindium could dissociate to $(CH_3)_2In^+$ and CH_3^-. The methyl anion would attack the central carbon of hexafluoroacetone, according to this theory, and the negatively charged oxygen could bond to indium:

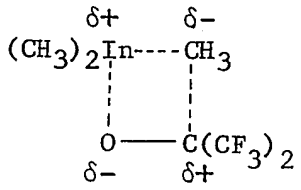
$$(CH_3)_3In \rightleftarrows (CH_3)_2In^+ + CH_3^- \qquad VIII$$

$$CH_3^- + O{=}C(CF_3)_2 \downarrow$$

$$^{-}O\text{-}C(CF_3)_2 \qquad IX$$
$$\quad\;\; |$$
$$\quad\;\; CH_3$$

$$(CH_3)_2In^+ + {}^{-}O\text{-}C(CF_3)_2CH_3 \rightarrow (CH_3)_2In\text{-}O\text{-}C(CF_3)_2CH_3 \qquad X$$

Alternatively, a four-centre mechanism could be invoked, allowing the insertion reaction to go in one step:



$$\rightarrow \quad (CH_3)_2In\text{-}O\text{-}C(CF_3)_2CH_3 \qquad XI$$

6.5 Dimethylthallium(III) Derivatives

A number of dimethylthallium(III) salts were prepared under anhydrous conditions to investigate the possibility of anion coordination. Some of the organotin compounds having anion interaction (e.g. trimethyltin nitrate [9] and perchlorate [6, 7]) are only stable under anhydrous conditions. Dimethylthallium nitrate, perchlorate, tetrafluoroborate, and sulphate, prepared in anhydrous methanol or tetrahydrofuran, appear to be ionic and identical to the compounds prepared under aqueous conditions. Exposure of the 'anhydrous' salts to moist air caused no apparent changes such as are readily observed in certain organotin derivatives [9]. The compounds had infrared spectra characteristic of regular, undistorted anionic species (very strong broad bands as listed): nitrate, 1350 cm^{-1}; perchlorate, 1050 cm^{-1}; tetrafluoroborate, 1020 cm^{-1}; and sulphate, 1060 cm^{-1}. Bridging or chelation will normally reduce the symmetry of the anionic group. For example, ionic perchlorate has T_d symmetry, but a bidentate or bridging perchlorato group has C_{2v} symmetry, and marked changes in the infrared spectrum

accompany this reduction in symmetry [9, 92]. However if all four oxygens were interacting or 'coordinating' with organometallic species, the symmetry would remain T_d. It is most improbable that this situation exists because of the range of anions investigated. Total interaction of all oxygen or fluorine atoms would result in a variety of coordinations about thallium in these derivatives. However only one thallium-carbon absorption has been noted, hence the C-Tl-C moiety is probably linear in all cases. Therefore the infrared observations are interpreted as signifying the presence of ionic anions and ionic dimethylthallium(III) species.

In order to examine the stereochemistry of the dimethylthallium(III) moiety more thoroughly, a number of other experiments were conducted. Although a dimethylthallium iodide-pyridine complex cannot be isolated, the iodide is very soluble in this solvent. The infrared spectrum of a saturated solution shows two peaks attributed to thallium-carbon stretching vibrations, at 535 and 470 cm^{-1}. Thus the C-Tl-C group must be bent. Drago [33] and Beattie and Cocking [38] have made the same observation on pyridine solutions of dimethylthallium perchlorate (peaks at 548 - 546 and 484 cm^{-1}).

The compound dimethylthallium perchlorate-phenanthroline was prepared shortly before Beattie and Cocking reported it [38] in a study of adducts of the dimethylthallium(III) ion. It also has a bent C-Tl-C skeleton [40] and two peaks in the infrared spectrum at 551 and 496 cm^{-1}.

One addition complex of dimethylthallium iodide was synthesized. Dimethylthallium iodide-phenanthroline crystallized from a pyridine

solution as yellow crystals. Its infrared spectrum has peaks at 540 and 490 cm^{-1} assigned to thallium-carbon stretching, and absorptions characteristic of coordinated phenanthroline. It may well be that the energy of chelation overcomes the lattice energy that presumably stabilizes the dimethylthallium halides. This crystal packing energy may prevent the formation of 1:1 adducts with monodentate Lewis bases, which lack chelation stabilization. Unfortunately the low solubility of the iodide-phenanthroline complex in common solvents hindered a further study of this derivative.

Dimethylthallium acetylacetonate [78] was prepared, and has already been discussed. In the preparation of this derivative some dimethylthallium acetate was identified. It was not clear whether there was acetate in the acetylacetone or whether the dimethylthallium acetylacetonate derivative decomposed somewhat. Such decomposition has been observed for certain acetylacetonate derivatives of mercury and lead [84].

Numerous researchers have commented upon the remarkable stability of the $(CH_3)_2Tl^+$ ion, and attribute this to the linear nature of the ion lowering the energy of the bonding sp orbitals. All the dimethylthallium(III) salts of strong acids are very stable, both thermally and chemically. However the infrared spectrum of dimethylthallium acetate (see Appendix II) has peaks at 550 and 493 cm^{-1} which can be assigned to asymmetric and symmetric thallium-carbon stretching frequencies, respectively. Thus a bent C-Tl-C structure may be present in this derivative. It is not possible to distinguish between ionic,

bidentate, and bridging acetate groups on the basis of infrared spectra because the symmetry is C_{2v} in all cases [54], and there are not significant shifts of the infrared absorptions in the various cases. Monodentate acetato groups do show a slight difference, the asymmetric $-CO_2-$ stretching mode is shifted to higher frequency and the symmetric $-CO_2-$ mode to lower frequency, compared to the positions in the spectrum of an ionic acetate compound (1578 and 1414 cm^{-1}, respectively [119]). In dimethylthallium acetate the appropriate absorptions are at 1542 and 1425 cm^{-1}, hence a unidentate acetato group is improbable. Unfortunately Deacon, Green, and Nyholm [56], who have also studied this compound, did not report the complete spectrum of the compound but based their suggestion that it may be ionic on the infrared spectrum of the acetate group and the fact that it is highly ionized in methanol. Thus, in view of the conflicting or uncertain evidence, the structure of dimethylthallium acetate should be carefully re-examined.

Chapter 7

METHYLINDIUM(III) DICHLORIDE AND DERIVATIVES

During the course of this research, increased interest in the chemistry of indium trihalide derivatives [120, 121] stimulated the idea that a monoalkyl indium dihalide compound would be a useful derivative to synthesize in order to compare the properties, particularly of Lewis base addition compounds, of the series $(CH_3)_nInCl_{3-n}$, where n varies from zero to three. In addition the analogous compound, methylgallium dichloride (dimer), has been reported [50], but there is considerable controversy over the existance of the [methylthallium(III)]$^{2-}$ moiety. Hart and Ingold [122] and Sarrach [123] found that they were unable to isolate alkylthallium dihalides as reported by Melnikov and Gratscheva [124]. Very recently, Okawara has cited the brief existance of methylthallium diacetate in solution, as identified by nuclear magnetic resonance spectroscopy [125], and later isolated it [126]. The synthesis of methylindium dichloride was further stimulated by the formation of methylindium dichloride-bipyridine from dimethylindium chloride and bipyridine in methanol solution.

Coates has reported the reaction of trimethylaluminum and trimethylindium with phenylphosphine, and phenyl- and methyl-arsine,

eliminating two equivalents of methane and forming coloured, involatile polymeric material [14]. He does not specifically suggest that a methylindium(III) derivative is formed, but does use the formulation $[(CH_3)Al\text{-}As(CH_3)]_x$ as an example of one product.

Methylindium dichloride was prepared from trimethylindium and two equivalents of hydrogen chloride in ether solution, in a Carius tube. It was also obtained by an exchange reaction between dimethylindium chloride and indium trichloride, in ether solution. It forms a liquid complex with diethyl ether from which the ether may be removed *in vacuo* at 80°C, leaving a white powder. The product was extracted with hot toluene, recrystallizing as white, needle-like crystals upon cooling. The molecular weight in nitromethane (see Table 9) is that of the formula weight, although the conductivity at 13 mho cm^2mole^{-1} in the same solvent indicates slight ionization.

Several other elements form such a series of alkyl-metal-halide compounds. Coates [1] has described the methyl-metal-chloride series for boron, aluminum, and gallium. Thus indium extends this range of derivatives, but the thallium series is incomplete. Trimethylthallium, dimethylthallium chloride, and thallium trichloride have been studied by many laboratories. Sarrach [123] attempted the isolation of methylthallium dichloride from dimethylthallium chloride and thallium trichloride. Both he and Hart and Ingold [122] recovered lower inorganic chlorides, $(TlCl_2)_2$ and $(Tl_2Cl_3)_2$, and several organic compounds. The alkylthallium(III) salt is probably formed, but is very unstable. Decomposition is facilitated by the thermodynamically favoured reduction

Table 9

Properties of Methylindium Dichloride and Derivatives

Compound	Molecular Weight			Conductance		Infrared	
	calc. g.	found g.	conc. M x 10^2	Λ_m mho cm $mole^{-1}$	conc. M x 10^3	In-CH_3 rock	ν In-C cm^{-1}
CH_3InCl_2	200.8	196	3.87 a	13.3	3.18 a	745 s bd 720 sh	523 m
CH_3InCl_2-bipyr	356.9	375	1.38 a	26.4	1.54 a	obscured	496 m 508 vw?
CH_3InCl_2-2pyr	358.9					720 sh (obscured)	512 m
CH_3InCl_2-terpyridine	434.0					obscured	522 m 510*w sh

a CH_3NO_2

s strong
m medium
w weak
vw very weak
bd broad
sh shoulder

* probably due to ligand

of Tl(III) to Tl(I), in the form of the thallium(I) halide.

In group IV, the tin series $(CH_3)_mSnCl_{4-m}$ (m varies from zero to four) has been investigated [36, 127] and the analogous germanium series is known [1]. In group II, the series $(CH_3)_xMCl_{2-x}$ (x varies from zero to two) have been prepared for M = zinc or mercury [1], but an organocadmium halide derivative has not yet been isolated [128].

A number of addition compounds of methylindium dichloride were synthesized. The identification of the bipyridine derivative, originally prepared from dimethylindium chloride, has been confirmed by preparing the complex from methylindium dichloride and bipyridine. The infrared spectrum of this product is identical to that of the original compound. A pyridine derivative, methylindium dichloride-dipyridine, has also been isolated. A further product, methylindium dichloride-terpyridine, was synthesized and may contain a six-coordinate indium atom.

Recently Carty [120, 121] has studied complexes of indium trihalides with a variety of Lewis bases. Most of these form either 1:2 or 1:3 complexes; for example indium trichloride forms complexes of the former type with triphenylphosphine and triphenylphosphine oxide, but of the latter type, 1:3, with pyridine and dimethylsulphoxide. Higher complexes with ammonia have been studied tensiometrically [129], $InCl_3$-2-, 3-, or 5-NH_3, for example. 1,2-Bis(diphenylphosphino)ethane (PP) forms a 1:1 complex, acting as a bidentate ligand and thus occupying two coordination sites. Carty suggests an ionic dimer formulation for this compound, $[InCl_2(PP)_2]^+ [InCl_4]^-$, similar to Nyholm's description

of $InX_3(AA)$ (where AA is o-phenylenebisdimethylarsine, and X is halogen) as $[InX_2(AA)_2]^+ [InX_4]^-$ [130]. Carty assigns a *trans*-trigonal bipyramidal structure to the chloride 1:2 complexes, and a *trans*-octahedral structure to the chloride 1:3 complexes. The stereochemistry of some other indium derivatives apparently differs, based upon interpretation of far infrared data: indium triiodide-bis(dimethylsulphoxide) may be an ionic dimer; indium tribromide-bis(triphenylphosphine) is a *cis*-trigonal bipyramid (by preliminary X-ray crystallography); and indium tribromide- and triiodide-bis(triphenylphosphine oxide) are unassignable structurally. Thus there is no obvious, simple rule governing the stereochemistry of these addition compounds.

Gallium halides do form 1:1 complexes with some ligands, and Carty maintains that a few 1:2 and 1:3 complexes are known [120]. Cotton *et al.* [89] report a series of thallium trihalide complexes of the general stoichiometry TlX_3L_2.

At the other end of the $(CH_3)_nInCl_{3-n}$ series is trimethylindium. Coates has studied 1:1 coordination complexes of trimethylindium [42] as part of his researches on trimethylgallium and other organometallic derivatives of group III. The following complexes of trimethylindium were reported, with their melting points: trimethylamine (66.2 - 66.4°C); trimethylphosphine (46.5°C); trimethylarsine (28.2 - 28.8°C); ammine (28.5 - 29.0°C); dimethylsulphide (19.0 - 19.5°C); and diethyl ether (liquid at room temperature). No higher complexes have been reported for trimethylindium. Complexes with secondary (and primary) amines,

phosphines, and arsines have been prepared, but readily lose methane, forming dimethylindium(III) derivatives.

In resumé, trimethylindium forms 1:1 adducts with monodentate ligands; dimethylindium chloride forms 1:1 complexes with monodentate ligands and also 1:1 compounds with bidentate ligands; methylindium dichloride forms a 1:2 addition compound with pyridine, a 1:1 complex with a bidentate ligand, and a 1:1 complex with a tridentate ligand; and indium trichloride yields both 1:2 and 1:3 complexes with monodentate Lewis bases. Thus the coordination about indium in these derivatives varies from four to five to six. In certain cases, the ionic dimers, indium atoms have four- and six-coordination in the same compound.

Although not a great number of analogous compounds of group III elements are known, it appears that the addition compounds of the methyl-indium-chloride system parallel the behaviour of analogous derivatives of the lighter elements of the group. Alkyl-aluminum-chloride derivatives form a series of complexes with ammonia [73]; the general trend being that the higher the number of chloride atoms, the higher the number of ammonia molecules possible (e.g. $AlCl_3$-3-, 5-, 6-, or 14-NH_3 [129]; $C_2H_5AlCl_2$-1-, 2-, or 5-NH_3; $(C_2H_5)_2AlCl$-1- or 2-NH_3; and R_3Al-NH_3 only [103] [which decomposes readily]). Complexes of diethyl-aluminum chloride with pyridine and trimethylamine are 1:1 compounds. Methyl-gallium-chloride complexes with ammonia have been mentioned earlier, and appear to be similar to the aluminum and indium compounds in some cases. In group III, the thallium derivatives are significantly

different. Although adducts of thallium trichloride are known, none have been reported for the questionable methylthallium dichloride, and dimethylthallium chloride does not form complexes with monodentate Lewis bases. Only dimethylthallium iodide-phenanthroline has been synthesized, and can be compared to dimethylindium chloride-phenanthroline. Trimethylthallium does form 1:1 complexes with donor ligands. Coates and Whitcombe [42] have established that the order of acceptor strength of group III trialkyls towards donor ligands (specifically trimethylamine) is B < Al > Ga > In > Tl.

Various addition compounds of the methyl-tin-chloride series have been reported by Beattie and McQuillan [35]. The first three members of the series, tin tetrachloride, methyltin trichloride, and dimethyltin dichloride, form 1:2 complexes with monodentate ligands and 1:1 complexes with bidentate ligands. Thus all of these derivatives attain six-coordination about tin. Trimethyltin chloride forms only a 1:1 complex with pyridine [10] or dimethylsulphoxide [132], giving a five-coordinated tin adduct. Tetramethyltin apparently does not give addition compounds with ligands [133].

Chapter 8

DISCUSSION

The synthesis of trimethylindium and certain dimethylindium(III) halide derivatives by means of reacting indium trichloride with methyllithium in ether solution has proved to be a most satisfactory synthetic route on the laboratory scale.

Numerous new dimethylindium(III) derivatives have now been prepared. Many of these may be allocated to a few general classes of dimethylindium(III) compounds: a) halides; b) 1:1 monodentate Lewis base adducts of the halides; c) anionic bidentate ligand derivatives; d) neutral bidentate ligand chelates of the halides; e) 'salts' or derivatives of acids in general; and f) complex anions. Other derivatives were synthesized and were either isolated compounds (e.g. dimethylindium hydroxide) or representative examples of other classes of derivatives (e.g. dimethyl(3,3,3-trifluoropropynyl)indium-etherate, representative of acetylide derivatives). These derivatives thus expand the number of organoindium compounds known, and facilitate a better understanding of organoindium chemistry. In addition, a more comprehensive comparison of the dimethyl derivatives of group III elements is now possible.

In general terms (i.e. stereochemistry and reactivity), organometallic derivatives of indium are very similar to those of gallium [50] and aluminum [1]. Certain compounds are also similar to the thallium analogues. Thus the following derivatives of dimethyl-aluminum(III), -gallium(III), -indium(III), and -thallium(III) form homologous series: methoxide, acetylacetonate, and certain amino- complexes. In less specific terms, dialkylmetal acetylides of gallium, indium, and thallium, and o-nitrophenoxides of indium and thallium, appear to be similar.

The trialkyls of group III elements are quite similar in their chemical reactions, both in forming 1:1 addition complexes with donor ligands and in being highly reactive towards oxidation and hydrolysis. The order of acceptor strength towards ligands is Al > Ga > In > Tl for the trialkyls [42]. Similarly, the first bond dissociation energy for the metal-carbon bond in the trialkyl-metal derivatives falls regularly: trimethylgallium, 60 kcal.; trimethylindium, 47 kcal.; and trimethylthallium, 27 kcal. [134].

Other derivatives form a homologous series of the aluminum, gallium, and indium derivatives, but the thallium analogues differ in some respects. These dimethylmetal derivatives include: halides, hydroxide, cyanide, acetate, 1:1 adducts of monodentate Lewis bases with halides (unknown for thallium), and the tetramethylmetal anion (unknown for thallium). Many 'salts' and β-diketone chelates of dimethylthallium(III) are known, but few comparisons can be made to other group III analogues.

Thus, although some series of analogous organometallic derivatives of group III are homologous, apparently being similar in structure and properties, other series of compounds show a marked change in the thallium derivative. That is, certain organometallic derivatives of aluminum, gallium, and indium form a homologous series, but the thallium analogue either has not been prepared or is distinctly different, usually appearing to be ionic. For example, the dimethylaluminum, -gallium, and -indium cyanides are tetrameric in benzene solution, but dimethylthallium cyanide is ionic in water and insoluble in benzene [41]. Apparently the dimethylthallium(III) group achieves considerable stability in the form of a linear cation, particularly in the solid state where crystal packing may result in effective six-coordination about thallium. Salts of dimethylthallium(III), other than halides, do form Lewis base addition complexes (e.g. dimethylthallium perchlorate-pyridine [38] and dimethylthallium tetraphenylborate-dipyridine [33]). Therefore the lack of formation of dimethylthallium halide-Lewis base adducts may be a result of the strong tendency of the halide ions to coordinate as ligands (or crystal stabilization energy) rather than an inherent weakness towards complex formation on the part of the dimethylthallium(III) species.

In terms of chemical reactivity and stability, the thallium-carbon bonds in dimethylthallium(III) derivatives are significantly more stable and resistant to oxidation or hydrolysis than are the indium-carbon and gallium-carbon bonds. The relative stability towards heat, hydrolysis, and oxidation of the former derivatives may account for the early study of organothallium compounds and the lack of interest

in organoindium chemistry.

The most common stereochemistry about indium in dimethylindium-(III) derivatives and other organoindium compounds is probably a distorted tetrahedral arrangement in most cases. This stereochemistry is often achieved by dimerization or a higher degree of association. 1:1 Complexes of dimethylindium halides with monodentate ligands, and some of the anionic bidentate ligand derivatives, already have four-coordinate indium, hence association is unnecessary and the compounds are found to be monomeric. Tetrahedral coordination appears to be normal for organoaluminum and organogallium derivatives, but both tetrahedral and (distorted) octahedral coordination may be common in the organothallium compounds.

Three-coordination occurs in many trialkyls of gallium, indium, and thallium, although trimethylindium does have a complex tetrameric structure with five-coordinate indium in the solid state [23]. Although the dimethylthallium(III) ion appears to have two-coordinate thallium, crystal packing in the solid state or solvation in solution [33] raises the actual coordination number.

Dimethylindium halide-bidentate ligand derivatives have been examined and a five-coordinate indium model has been invoked to explain the structure. Except for dimethylthallium iodide-phenanthroline, the structure of which is unknown, analogous gallium and thallium derivatives are not available for comparison. Dimethylthallium perchlorate-phenanthroline has been shown to have six-coordinate thallium, with

weakly bridging perchlorate groups [40].

The methyl-indium-chloride series, from trimethylindium through successive substitution to indium trichloride, exhibits chemical and stereochemical behaviour similar to that observed in other metals, such as aluminum [73] or tin [35]. Indium trihalides readily achieve six-coordination with either neutral or anionic ligands (e.g. indium trichloride-tripyridine or $InCl_6^{3-}$), and five-coordination about indium is also known (e.g. indium trichloride-bis(triphenylphosphine))[121]. The structure of methylindium dichloride is uncertain, but complexes with pyridine and bipyridine, if monomeric and unassociated, would have five-coordinate indium. Methylindium dichloride-terpyridine may have six-coordination about indium. Dimethylindium halides form only four-coordinate species with donor ligands (e.g. pyridine, triphenylarsine oxide and triphenylphosphine oxide) and five-coordinate species with bidentate ligands (e.g. 1,10-phenanthroline and 2,2'-bipyridine), and the highest coordination about indium in trimethylindium is five in the crystal or four in 1:1 complexes with Lewis bases.

This trend in coordination is seen even more clearly in the tin series [35, 116]. Fortunately a large number of tin derivatives are available for comparison purposes. The $SnCl_6^{2-}$ ion and tin tetrachloride-dipyridine are examples of maximum (six) coordination about tin. Methyltin trichloride and dimethyltin dichloride also form six-coordinate complexes (e.g. methyltin trichloride-dipyridine and dimethyltin dichloride-phenanthroline [35]), giving octahedrally coordinated tin. However trimethyltin chloride only forms stable five-coordinate species.

The 1:1 Lewis base adducts of trimethyltin halides may be compared to those of the dimethylindium halides. However the trimethyltin halides also form 1:2 adducts. Both 1:1 and 1:2 complexes have five-coordinate tin. Trimethyltin 8-hydroxyquinolinate and dimethyltin chloride 8-hydroxyquinolinate, with a five-coordinate metal atom, are analogous to dimethylindium chloride-phenanthroline or -bipyridine. Apparently four is the highest coordination number for tin in tetramethyltin, no addition complexes having been reported. Tetramethyltin is both isoelectronic and likely isostructural to the tetramethylindate anion. Hence the organometallic derivatives of indium bear a distinct similarity to those of tin, providing the difference in charge is taken into account.

One common factor in the trend of coordination number of the metal in these cases is the variation in charge density on the metal atom. In strictly qualitative terms, chloride is electronegative relative to methyl carbon or ligand nitrogen [135]. Thus chloride atoms will lower the charge density on the metal, and methyl groups or Lewis bases will increase the charge or electron density on the metal. It remains unclear how this behaviour effects the energy levels and symmetry of molecular orbitals involving indium. However, when the number of electronegative groups about a metal such as indium is increased, the maximum possible coordination number is also increased relative to that for a metal surrounded by electropositive groups, as in trimethylindium or the tetramethylindate anion.

Very little is known about organocadmium chemistry, and hence

comparisons to organoindium derivatives cannot be made. There are, however, certain similarities between organomercury and organothallium derivatives. Both the methylmercury and dimethylthallium halides have effective six-coordination about the metal in the solid state, and both series of derivatives apparently do not form 1:1 adducts with monodentate donor ligands. The metal-carbon bonds in these compounds are relatively unreactive, and the derivatives are stable to hydrolysis and oxidation. Conversely many organolead compounds tend to decompose rather readily. Further, some organometallic derivatives of the heavy metals gold, thallium, and lead share the common property of being light sensitive, and may decompose upon exposure to visible or ultraviolet radiation.

A common feature of the dimethyl derivatives of group IIB and the trimethyl derivatives of group III is the reactivity of at least one methyl group towards oxidation or in undergoing exchange (i.e. with another alkyl group or with a halide derivative of a metal). Methyl exchange can be a very useful phenomenon. For example, dimethylmercury and dimethylzinc have long been used to prepare methyl derivatives of other metals. Trimethylindium undergoes exchange with one-half equivalent of indium trichloride, yielding dimethylindium chloride, which in turn will exchange with a mole of indium trichloride to yield methylindium dichloride.

The reactivity of trimethylindium with compounds containing available hydrogen appears to represent another common feature of the

group III trialkyls. Coates [1, 14, 37] has described the reaction of trimethyl-aluminum, -gallium, and -indium with secondary amines, phosphines, and arsines, and certain oxy- and thio-acids. All reactions yield methane and associated dimethylmetal derivatives. Triethylgallium reacts with terminal acetylenes, eliminating a mole of ethane and forming a diethylgallium acetylide [106]. A recent report [136] has described the reaction of triethylthallium with triethylgermane:

$$3(C_2H_5)_3GeH + (C_2H_5)_3Tl \xrightarrow[100°C]{} 3C_2H_6\uparrow + [(C_2H_5)_3Ge]_3Tl \qquad I$$

This reaction is interesting not only as an example of the reaction of a thallium trialkyl with available hydrogen, but also because of the metal-metal bonds formed and, by using a temperature of 100°C, the fact that all three thallium-ethyl bonds are cleaved. In numerous reactions trimethylindium readily loses one methyl group by reaction at or below 24°C, but a second methyl group is eliminated only very slowly. By mixing appropriate stoichiometrical quantities of reagents, either two or three equivalents of hydrogen-containing reagent to one of trimethylindium, and raising the temperature, the synthesis of di- and tri-substituted (organo)indium compounds may be realized.

It should be understood that the inability to synthesize certain derivatives, such as dimethylindium chloride-dipyridine, in no way precludes the existence of these compounds. Several examples support this statement. Deacon [96] could only prepare bis(pentafluorophenyl)thallium acetate-bipyridine from a solution containing a large excess (eight-fold) of bipyridine. Attempted recrystallization of the

complex from aqueous methanol resulted in decomposition to the original reactants. Methylthallium(III) derivatives exist, but readily decompose to thallium(I) salts, making isolation of the compounds difficult. (Dimethylamino)dimethylthallium could not be synthesized from trimethylthallium and dimethylamine, but was prepared from dimethylthallium bromide and (dimethylamino)lithium [42]. Gallium tribromide reacts with pyridine *in vacuo* to give 1:1 and 1:2 adducts, but the 1:3 complex is only obtained from an ethanolic solution of the reactants [120]. Therefore it may prove necessary to try various methods of synthesis to obtain certain compounds.

In many instances the compounds or reactions investigated here warrant further study. Numerous problems have been raised by many of the results or observations, and there is opportunity for extensive research in the field of organoindium chemistry. Only a few of the more important possible topics will be mentioned here. Dimethylindium 'salts', such as the nitrate, tetrafluoroborate, and sulphate, and their addition complexes with Lewis bases, could prove interesting in comparison with the thallium analogues and the methyl-tin derivatives. The structures of certain derivatives, particularly dimethylindium fluoride and chloride, and dimethylindium chloride-phenanthroline or -bipyridine, should be determined by X-ray crystallography. Methylindium dihalide derivatives may be useful for kinetic or mechanistic studies of halide or methyl exchange with other indium derivatives. Only one organometallic compound of indium(I) has been synthesized

(InC_5H_5, [137, 138]). The possibility of other organic groups stabilizing indium in the univalent state could bear investigation. Metal-metal bonded compounds containing indium have recently been reported [139], and it is highly likely that organoindium species will form such metal-metal bonded compounds. Many examples are known for organotin derivatives. The electronegative nature of the trifluoromethyl group relative to methyl (cf. pentafluorophenyl compared to phenyl) makes the preparation of trifluoromethylindium derivatives an attractive project, particularly for the stereochemical elucidation of the influence of electronegativity on coordination and structure. The brief study of dimethylthallium(III) derivatives, and comparisons to dimethylindium(III) compounds, included in this thesis suggest that further extensive investigation of dialkylthallium(III) chemistry is needed to determine under what conditions dimethylthallium(III) compounds resemble, or differ from, other group III analogues.

Chapter 9

EXPERIMENTAL

All operations (except conductance and molecular weight studies) were carried out in a glass vacuum system or under nitrogen in a dry box or glove bag. Chemicals and solvents were dried by standard methods, and glassware was oven-dried. The methyllithium (Foote Mineral Company) was prepared from methyl chloride, and hence was free of halide. Infrared spectra sere taken on a Beckman IR 10 spectrophotometer (4000 - 300 cm^{-1}, calibrated against polystyrene) in nujol or halocarbon oil mulls between potassium bromide or cesium iodide plates. Molecular weights were measured in benzene or nitromethane solution of a Mechrolab Vapor Phase Osmometer model 301A. Conductance studies were done in methanol or nitromethane using an Industrial Instruments Conductivity Bridge and a conductivity cell with cell constant 0.100 cm^{-1}. Nuclear magnetic resonance spectra were recorded on a Varian Associates A-60 spectrometer. Analyses were by Dr. Alfred Bernhardt, Dr. A. B. Gygli, or Schwarzkopf Microanalytical Laboratory. Some chloride analyses were determined by the dichlorofluorescein adsorption indicator method [140], after oxidation of a sample with aqueous hydrogen peroxide and removal of indium as the hydroxide. All

products were white crystalline solids unless otherwise stated.

Melting points (uncorrected), given in degrees centigrade, were measured in sealed tubes in a Hoover capillary melting point apparatus. In numerous instances, compounds did not have distinct melting points but appeared to soften or partially melt over a wide temperature range. Beachley, Coates, and Kohnstam [141] have studied compounds of the series $[(CH_3)_2M\text{-}N(CH_3)_2]_2$, (where M is aluminum, gallium, or indium) and have observed that these derivatives have two forms. At room temperature the compounds are crystalline solids, but at higher temperatures (50 - 75°) they are transformed into glasses. These glasses then 'melted' over a temperature range of several degrees (in the region of 150 - 175°). Therefore it is possible that some of the organoindium derivatives reported here are exhibiting this type of phase transition. Alternatively, compounds, particularly addition complexes, may be decomposing over a wide temperature range and not actually melting.

Trimethylindium

Indium trichloride (1.2 g., 5.5 mmoles) was mixed with methyllithium (10 ml. at 1.67 M, 16.7 mmoles) in 10 ml. of ether. After the vigorous reaction was complete the ether and trimethylindium were condensed into a -196° trap *in vacuo*, while the reaction vessel was heated to 80° to increase the rate of transfer of the final product. Transfer was complete in 45 minutes. Due to the difficulty of separating trimethylindium quantitatively from ether, fractional distillation

was not normally attempted. Virtually no indium remained in the involatile residue, as determined by acid hydrolysis followed by neutralization with ammonium hydroxide to precipitate indium hydroxide. Hence the yield of trimethylindium was nearly quantitative. A sample for analysis was obtained by repeated fractional distillation. (Found: C, 21.54; H, 5.21. C_3H_9In calcd.: C, 22.54; H, 5.74%)

Dimethylindium Halides

a) Indium trichloride (1.5 g., 6.8 mmoles) was mixed with methyllithium (8.1 ml. at 1.67 M in ether, 13.6 mmoles) in 20 ml. of ether and shaken for two days. Volatile components were removed *in vacuo*, and dimethylindium chloride was purified by sublimation at 110° *in vacuo* to a 15° cold finger, forming a white powder or colourless crystals. Yield 1.0 g., 81%; melting point 218 - 219°. (Found: C, 13.67; H, 3.51; Cl, 19.22. C_2H_6ClIn calcd.: C, 13.32; H, 3.35; Cl, 19.66%)

This experiment was repeated with the same quantities of reagents, but all volatile components were removed immediately after the vigorous reaction ceased (approximately 30 minutes). The product was trimethylindium. No dimethylindium chloride was formed, but the involatile residue contained indium. The trimethylindium was recombined with the residue in ether solution, and dimethylindium chloride was recovered after two days.

b) Dimethylindium iodide was prepared when indium trichloride (1.0 g., 4.5 mmoles), methyllithium (5.4 ml. at 1.67 M, 9.0 mmoles), and lithium iodide (0.6 g., 4.5 mmoles) were mixed in 20 ml. of ether and shaken for two days. After thorough pumping *in vacuo*, the product

was purified by sublimation *in vacuo* as above. Yield 0.9 g., 73%; melting point 212 - 218°. (Found: C, 9.09; H, 2.49. C_2H_6IIn calcd.: C, 8.84; H, 2.23%)

Dimethylindium iodide (0.2 g., 0.7 mmoles) and methyllithium (0.5 ml. at 1.67 M, 0.8 mmoles) were mixed in ether. Following vacuum fractionation, trimethylindium was identified by its infrared spectrum [45].

c) Dimethylindium bromide was synthesized by condensing hydrogen bromide (4.6 mmoles) onto a solution of dimethylindium methoxide [42] in ether solution. The product was purified by subliming twice *in vacuo* at 110°. Melting point 210° with decomposition. (Found: C, 10.1; H, 2.65. C_2H_6BrIn calcd.: C, 10.7; H, 2.69%)

d) Dimethylindium fluoride precipitated with effervescence when boron trifluoride-etherate (0.26 g., 1.8 mmoles) in ether was slowly added to trimethylindium (*ca.* 5.4 mmoles) in ether solution. The product was sublimed *in vacuo* at 130 - 140° (yield 0.5 g., *ca.* 50%), recrystallized twice from methanol and resublimed. The compound began to melt and decompose at 295°. (Found: C, 14.87; H, 3.81; F, 11.98. C_2H_6FIn calcd.: C, 14.67; H, 3.70; F, 11.60%)

Certain additional observations on synthetic methods or reagents used in the above reactions are worth comment. The methyllithium (Foote Mineral Company) used throughout was prepared from methyl chloride and was free of halide. It was used as a 5% (1.67 M) solution in ether. A sample of methyllithium as a suspension in heptane was used for initial studies, but gave very poor and inconsist-

ent results. This reagent was found to contain nearly 60% lithium iodide, corresponding approximately to the formula $(CH_3Li)_2$-LiI. Dimethylindium halides decomposed slowly when stored in a desiccator or dry box, but samples could be kept indefinitely in evacuated vessels. In the preparation of trimethylindium in ether an excess of methyllithium beyond the 3:1 stoichiometrical ratio (methyllithium : indium trichloride) must be avoided to prevent formation of lithium tetramethylindate. Slight oxidation or hydrolysis of trimethylindium in ether may lead to a mixture of oily, sublimable decomposition products, as noted by Dennis *et al.* [22] in the original preparation of the compound. A slight trace of such byproducts was occasionally observed in sublimed samples of dimethylindium halides. These may be eliminated by exposing the crude halide to air for a few minutes prior to sublimation.

Lewis Base Adducts of Dimethylindium Halides

These derivatives were prepared by mixing dimethylindium chloride or iodide with one equivalent of the Lewis base (except pyridine, which was used in excess or as the solvent) in solution.

a) Dimethylindium chloride-pyridine was precipitated when pyridine was added to dimethylindium chloride in ether solution. The product was purified by washing with ether. Melting point 82 - 84.5°. (Found: C, 31.88; H, 4.21; Cl, 14.6. $C_7H_{11}NClIn$ calcd.: C, 32.41; H, 4.27; Cl, 13.67%)

b) Dimethylindium iodide pyridine was prepared from the iodide in pyridine solution. Excess pyridine was pumped off and the product

purified by sublimation *in vacuo* at 60°. Melting point 72 - 75°. (Found: C, 24.17; H, 3.10. $C_7H_{11}NIIn$ calcd.: C, 23.96; H, 3.16%)

c) Dimethylindium iodide-triphenylphosphine was prepared from ether solution and washed with a little ether and petroleum ether. (Found: C, 44.86; H, 3.82. $C_{20}H_{21}PIIn$ calcd.: C, 44.98; H, 3.96%)

d) Dimethylindium chloride-triphenylphosphine oxide was recovered as a gum from ether/chloroform solution. It was recrystallized from the ternary solvent system chloroform/ether/petroleum ether (80-100). The compound softened at 55° and melted at 95°. (Found: C, 51.60; H, 4.53. $C_{20}H_{21}POClIn$ calcd.: C, 52.38; H, 4.62%)

e) Dimethylindium chloride-triphenylarsine oxide also formed a gum upon concentration of an ether/chloroform solution. It crystallized upon trituration. The compound was recrystallized from ether/chloroform/petroleum ether (80-100) yielding colourless needle-like crystals. It is soluble in methanol and benzene. The complex softened at 63° and melted at 97 - 99°. (Found: C, 47.29; H, 4.06. $C_{20}H_{21}AsOClIn$ calcd.: C, 47.81; H, 4.21%)

f) Dimethylindium iodide-triphenylphosphine oxide was prepared as a white, gummy substance from ether solution. The infrared spectrum was similar to that of the gummy form of dimethylindium chloride-triphenylphosphine oxide. The compound was dissolved in ethanol and silver nitrate solution added, causing precipitation of silver iodide. The solvent was removed *in vacuo* leaving a gummy substance containing nitrate, dimethylindium(III), and triphenylphosphine oxide species according to the infrared spectrum.

g) Dimethylindium iodide is very soluble in acetonitrile, but the solvent is readily removed *in vacuo* and the iodide is recovered unchanged.

h) Dimethylindium chloride absorbs tetrahydrofuran vapour exothermally, yielding a liquid at room temperature. The tetrahydrofuran may be removed *in vacuo*.

i) Both dimethylindium chloride and iodide are very soluble in diethyl ether and can be recrystallized from this solvent.

j) Bis[dimethylindium chloride]-triphenylphosphine was recovered from an equimolar mixture of dimethylindium chloride and triphenylphosphine in ether solution. It crystallizes during concentration of the solution, leaving excess triphenylphosphine in solution. A 2:1 mixture (chloride to phosphine) in ether solution yielded a white crystalline solid when the solution was evaporated to dryness. The infrared spectrum of this product was identical to that of the previous product, and showed no indications of unreacted starting materials. However recrystallization of a 2:1 mixture (chloride to phosphine) from ether/toluene resulted in the formation of lustrous plates of dimethylindium chloride. Uncomplexed triphenylphosphine was recovered from the supernate liquid. The 2:1 complex softened and melted over the temperature range 138 - 148°. N.m.r. spectra (see Appendix III) at 37° and -30° in various solvents showed only a single sharp indium-methyl proton signal in the region 9.85 - 10.14 τ. (Found: C, 41.79; H, 4.30. $C_{22}H_{27}PCl_2In_2$ calcd.: C, 42.4; H, 4.37%)

Ammonia Complexes of Dimethylindium Chloride and Iodide

Complexes of ammonia were studied tensiometrically. A known amount of dried ammonia (measured by pressure, volume, and temperature) was admitted to a vessel containing dimethylindium iodide or chloride. The pressure of the ammonia was recorded when it had apparently reached equilibrium. The time for equilibration varied between a few minutes at less than a 1:1 ratio of halide to ammonia to a few days at a ratio of 1:2. At higher pressures (i.e. at higher ammonia to halide ratios) the measured pressure is very temperature dependent. A plot of pressure of ammonia against moles of ammonia was made for the empty reaction vessel. Details of properties and tensiometric results are given in Table 4 and Figure 3.

Anionic Ligand Derivatives of Dimethylindium(III)

These derivatives were synthesized by mixing one equivalent of the 'ligand' reagent with trimethylindium in ether solution.

a) Dimethylindium acetylacetonate [42] was prepared from acetylacetone and trimethylindium. It was purified by sublimation *in vacuo* at 55° after the volatiles were pumped off. Melting point 132 - 134°. (Found: C, 35.12; H, 5.66. $C_7H_{13}O_2In$ calcd.: C, 34.47; H, 5.37%)

b) Dimethylindium 8-hydroxyquinolinate was precipitated with effervescence as a bright yellow solid when 8-hydroxyquinoline in ether was added to trimethylindium in ether solution. The compound decomposed around 260°, and appears to be air stable. (Found: C, 46.16; H, 4.58. $C_{11}H_{12}NOIn$ calcd.: C, 45.7; H, 4.18%)

c) Dimethylindium o-nitrophenoxide was precipitated slowly as a bright orange solid from an ethereal solution of trimethylindium and o-nitrophenol. The compound decomposed at 193 - 196°. (Found: C, 33.81; H, 3.89. $C_8H_{10}O_3NIn$ calcd.: C, 33.9; H, 3.56%)

d) Trimethylindium and 2-aminoethanethiol were mixed in ether and stored for three days. The thiol is scarcely soluble in ether. A non-condensable gas (probably methane) was slowly evolved. The final product was a light orange solid insoluble in all common solvents, and could not be purified. The analysis did not conform to that expected for dimethylindium 2-aminoethane sulphide. The substance appeared to decompose above 170°. (Found: C, 17.12; H, 4.01. $C_4H_{12}NSIn$ calcd.: C, 21.74; H, 5.47%)

Bidentate Ligand Derivatives of Dimethylindium Halides

These derivatives were prepared by the same method used to synthesize the 1:1 adducts of monodentate Lewis bases and dimethylindium halides. The reactants were mixed in a stoichiometrical ratio of 1:1 in solution, and the products purified by recrystallization.

a) Dimethylindium chloride-phenanthroline was isolated from an ether solution of dimethylindium chloride and dried, sublimed phenanthroline. Crystallization occurred slowly after the solution had been concentrated. Yield 80%; melting point 207 - 210° with decomposition. (Found: C, 46.48; H, 3.78; Cl, 9.96. $C_{14}H_{14}N_2ClIn$ calcd.: C, 46.64; H, 3.91; Cl, 9.83%)

b) Dimethylindium chloride-bipyridine formed a gummy precipitate

when the reactants were mixed in ether solution. This crystallized upon concentration of the solution and trituration. The compound slowly melted over the range 109 - 115°. (Found: C, 44.28; H, 4.32. $C_{12}H_{14}N_2ClIn$ calcd.: C, 42.84; H, 4.19%) An attempt to prepare this compound from methanol solution yielded some methylindium dichloride-bipyridine.

c) Dimethylindium iodide-bipyridine was isolated from a methanol solution of the iodide and bipyridine following evaporation of the solvent *in vacuo*. The light yellow compound was recrystallized from chloroform/toluene. It was also prepared from an ethereal solution of the two reactants, yielding a light yellow-green precipitate. Melting point 122 - 125°. (Found: C, 33.63; H, 3.42. $C_{12}H_{14}N_2IIn$ calcd.: C, 33.68; H, 3.30%)

d) Dimethylindium chloride-ethylenediamine was prepared by mixing dimethylindium chloride in slight excess with ethylenediamine in methanol solution. The compound was recrystallized from methanol/chloroform. It was also recovered from methanol solution by successive treatment with petroleum ether causing precipitation of the complex. The compound began to melt and decompose over the range 135 - 145°. (Found: C, 19.92; H, 5.44; Cl, 14.92. $C_4H_{14}N_2ClIn$ calcd.: C, 19.99; H, 5.87; Cl, 14.75%) An unidentified byproduct of low solubility in methanol/chloroform was produced during recrystallization. A slight excess of ethylenediamine resulted in a different product, likely a solvate. It had certain additional absorptions in the infrared spectrum compared to the spectrum of the 1:1 adduct. Typical analyses for this product are: C, 21.07; H, 6.17; Cl, 13.35, 14.38, 12.78, 15.86%. This

complex was also obtained by adding ethylenediamine to an ether solution of dimethylindium chloride, causing precipitation of a bulky white solid.

e) Dimethylindium iodide-ethylenediamine was also prepared and purification was again difficult due to the formation of a solvate. The complex softened and melted with decomposition in the range 172 - 184°. (Found: C, 16.77, 15.91; H, 5.24, 4.94. $C_4H_{14}N_2IIn$ calcd.: C, 14.48; H, 4.25%)

Miscellaneous Derivatives

a) 3,3,3-Trifluoropropyne was prepared from 1,1,2-trichloro-3,3,3-trifluoropropene-1 and zinc according to the method of Finnegan and Norris [142]. An excess of the propyne was added to an ethereal solution of trimethylindium in a Carius tube, which was sealed. The tube was heated to 100° for a few hours. The solution turned dark brown and white, needle-like crystals of dimethylindium fluoride appeared. Upon fractional distillation of the solution a small amount of a slightly volatile, colourless liquid was obtained. An infrared spectrum, and proton and fluorine magnetic resonance spectra, were obtained. These results, the presence of ether, methyl-indium, and trifluoromethyl species, suggest that the compound is dimethylindium(3,3,3-trifluoropropynyl)indium-etherate. It is extremely sensitive to oxygen and water, and its ready decomposition in a sealed tube or in chloroform or ether solution may indicate that it is also light sensitive. Decomposition occurred too rapidly for analyses to be performed.

b) Acetone was condensed onto trimethylindium in ether in a Carius tube, at -196°. A white precipitate appeared in the sealed tube after a few days at room temperature, and methane was evolved. The solid was collected and identified as methylindium oxide by its infrared spectrum. The solution was fractionally distilled, leaving a whitish gum. Upon heating to 100° *in vacuo* this yielded a trace of clear, colourless liquid on a cold finger sublimer. The infrared spectrum indicates that acetone is present, but likely complexed. Hence a dimethylindium(III)-acetone compound is likely formed, but rapidly decomposes to methylindium oxide.

c) Dimethylindium methoxide [42] was prepared from methanol and trimethylindium in ether solution. It is a viscous liquid.

d) Dimethylindium hydroxide was formed from trimethylindium and one equivalent of water in ether solution at -40°. It is a white powder, soluble in ether and slightly soluble in benzene. Methane is rapidly evolved, yielding methylindium oxide within a few hours.

e) Methylindium oxide is also the final product of decomposition of trimethylindium in ether solution when exposed to air and water. It is an involatile, insoluble white powder which may be decomposed by dilute acid. The compound appeared to decompose slightly at 255°, but did not melt. (Found: C, 8.05; H, 1.85. CH_3OIn calcd.: C, 8.23; H, 2.07%)

f) The preparation of bis(dimethylindium)oxide was attempted by mixing two equivalents of trimethylindium with one of water in ether solution. Immediate fractional distillation of the solution yielded

unreacted trimethylindium in the volatile fraction, and dimethylindium hydroxide in the involatile residue. Storing of the 2:1 mixture in a sealed Carius tube resulted in methylindium oxide precipitating after one day, and some trimethylindium was again recovered.

Dimethylindium(III) 'Salts'

a) Dimethylindium acetate precipitated with effervescence from an ethereal solution of trimethylindium and excess acetic acid. It was purified by sublimation *in vacuo* at 130°. The compound is insoluble in benzene and just slightly soluble in nitromethane. It appeared to melt and decompose over the range 194 - 219°. (Found: C, 23.17; H, 4.29. $C_4H_9O_2In$ calcd.: C, 23.56; H, 4.55%)

b) Dimethylindium trifluoroacetate was prepared in a similar manner. It is soluble in warm ether but forms needle-like crystals when a solution is concentrated and cooled. It sublimes rapidly at 100° *in vacuo*. Melting point 220 - 222°. (Found: C, 18.98; H, 2.33; F, 22.05. $C_4H_6F_3O_2In$ calcd.: C, 18.83; H, 2.34; F, 22.10%)

c) The preparation of dimethylindium nitrate, perchlorate, and tetrafluoroborate was attempted by mixing dimethylindium chloride with silver nitrate, perchlorate, or tetrafluoroborate in methanol solution. All three reactions yielded white precipitates of silver chloride, but the first two quickly turned black. The silver tetrafluoroborate is very soluble in methanol, and was slowly added in solution to a solution of dimethylindium chloride. In the other two cases, solid or excess silver nitrate or perchlorate was present when the solutions went black.

Filtration and evaporation of the solutions yielded white or gray powders which gave poor infrared spectra. An n.m.r. spectrum of the tetrafluoroborate derivative exhibited a proton signal at 10.0 τ, in the region of methyl-indium proton signals (see Appendix III).

Thallous nitrate and sulphate were shaken with dimethylindium iodide in methanol for several days, and some yellow thallous iodide was produced. However the insolubility of the thallous salts, together with the coating effect of the thallous iodide over the thallous salts, prevented complete reaction when the reactants were mixed in a stoichiometrical ratio of 1:1. The solids from evaporation of the solutions were similar to the former products.

An equilibrium or exchange reaction between trimethylindium and indium sulphate in ether was attempted by shaking the reactants for three days. The starting materials were recovered essentially quantitatively.

Organoindium Anions

a) Lithium tetramethylindate was synthesized by condensing trimethylindium onto methyllithium in ether at -196° *in vacuo*. The compound is very sensitive to oxidation and hydrolysis, and this may explain the poor analyses. (Found: C, 25.07; H, 6.40. $C_4H_{12}LiIn$ calcd.: C, 26.42; H, 6.65%)

b) Tetraphenylarsonium dimethylindium dichloride slowly crystallized when an ether/chloroform solution of tetraphenylarsonium chloride and dimethylindium chloride was concentrated. Melting point 148 - 152°. (Found: C, 51.81; H, 4.55; Cl, 11.88. $C_{26}H_{26}AsCl_2In$ calcd.:

C, 52.13; H, 4.37; Cl, 11.83%)

c) Similarly tetraethylammonium dimethylindium dichloride was prepared from methanol solution. It precipitated as a white solid upon addition of ether. In cold ether it is a white solid, but on warming it becomes a white, gummy substance in ether. The compound softened and melted over the range 41 - 62°. (Found: C, 32.74; H, 7.57; Cl, 21.56. $C_{10}H_{26}NCl_2In$ calcd.: C, 34.71; H, 7.57; Cl, 20.49%)

Insertion Product

Trimethylindium reacted with hexafluoroacetone in ether solution, yielding a clear, colourless liquid of very low volatility. It was purified by condensation onto a cold finger sublimer *in vacuo*. The infrared spectrum indicates the presence of dimethylindium and hexafluoroacetone species. Proton magnetic resonance shows two signals in the ratio of 2:1 at 9.91 τ ($-In(CH_3)_2$) and at 8.48 τ ($-C(CF_3)_2CH_3$). Thus the compound is thought to be dimethylindium 1,1-bis(trifluoromethyl)ethoxide. (Found: C, 21.3; H, 2.51; F, 33.19. $C_6H_9F_6OIn$ calcd.: C, 22.1; H, 2.78; F, 35.0%)

Methylindium Dichloride and Derivatives

a) Methylindium dichloride was prepared by two routes. Trimethylindium and two equivalents of hydrogen chloride were mixed in a Carius tube which was sealed and stored for two days. Ether and methane were removed *in vacuo* leaving a white solid after extensive pumping and heating to 80° to remove the last of the ether. This solid, a mixture of methylindium dichloride and indium trichloride, was extracted with

hot toluene to isolate the compound, which is soluble in boiling toluene but scarcely soluble in cool toluene. Alternatively indium trichloride and dimethylindium chloride were mixed in a 1:1 ratio in ether and stored for a day. The indium trichloride slowly dissolved. Methylindium dichloride was formed quantitatively. Melting point 165°. (Found: C, 6.06; H, 1.91, 2.45; Cl, 34.38. CH_3Cl_2In calcd.: C, 5.98; H, 1.51; Cl, 35.32%)

b) Methylindium dichloride-dipyridine was synthesized from methylindium dichloride and excess pyridine in ether solution. It was recrystallized from ether. This derivative is much more soluble in ether than indium trichloride-tripyridine. It softened at 75°, and turned to a cloudy gum by 116°. (Found: C, 37.30; H, 4.24; Cl, 19.85. $C_{11}H_{13}N_2ClIn$ calcd.: C, 36.81; H, 3.65; Cl, 19.76%)

c) Methylindium dichloride-bipyridine was obtained from the dichloride and bipyridine in ether solution. It precipitates as a fine white powder. The compound was also obtained from dimethylindium chloride (0.68 g., 3.8 mmoles) and bipyridine (0.30 g., 1.9 mmoles) in methanol solution. It slowly precipitates as white, needle-like crystals (0.31 g., 0.8 mmoles). It started to melt at 197° and decomposed around 224°. (Found: C, 36.83, 36.90, 37.02; H, 3.12, 3.43, 3.62; Cl, 19.81. $C_{11}H_{11}N_2Cl$ In calcd.: C, 37.02; H, 3.11; Cl, 19.86%)

d) Methylindium dichloride-terpyridine precipitated as a fine yellow powder from an ether solution of the dichloride and terpyridine. It was recrystallized from methanol. The compound did not melt below

260°. (Found: C, 42.91, 43.43; H, 3.70, 3.48; Cl, 15.97. $C_{16}H_{14}N_3Cl_2In$ calcd.: C, 44.28; H, 3.25; Cl, 16.37%)

Dimethylthallium(III) Salts and Derivatives

a) Dimethylthallium iodide was prepared according to the method of Gilman and Jones [143].

b) Dimethylthallium nitrate, perchlorate, tetrafluoroborate, carbonate, and sulphate were synthesized in anhydrous methanol or tetrahydrofuran solution from dimethylthallium iodide and the appropriate silver salt. Infrared spectra of these derivatives were identical with spectra of the salts made under aqueous conditions.

c) Dimethylthallium acetylacetonate [78] was prepared from dimethylthallium hydroxide or carbonate and acetylacetone in methanol solution. The initial product was a mixture of the acetylacetonate and the acetate, according to the infrared spectrum. The compound was purified by recrystallization and sublimation. Melting point 226° (literature value 214 - 215° [78]). (Found: C, 24.69; H, 4.25. $C_7H_{13}O_2Tl$ calcd.: C, 25.2; H, 3.93%)

d) Dimethylthallium acetate was prepared from dimethylthallium carbonate and acetic acid in refluxing ethanol. Although the infrared spectrum showed peaks attributed to dimethylthallium(III) and acetate species only, the analyses were not good. Therefore some thallous acetate may have been present. The product decomposed around 267°. (Found: C, 13.65; H, 2.00. $C_4H_9O_2Tl$ calcd.: C, 16.36; H, 3.09%)

e) Dimethylthallium perchlorate-phenanthroline was synthesized by

mixing dimethylthallium perchlorate and 1,10-phenanthroline monohydrate in acetone. It was identified by its infrared spectrum.

f) Dimethylthallium iodide-phenanthroline was also synthesized from acetone or pyridine solution. It is soluble in pyridine, and was recrystallized from this solvent yielding light yellow crystals. At the melting point, 216 - 217°, the compound decomposed to a brown liquid. (Found: C, 31.17; H, 2.68. $C_{14}H_{14}N_2ITl$ calcd.: C, 31.05; H, 2.61%)

APPENDIX I

SOME ORGANOINDIUM COMPOUNDS REPORTED IN THE LITERATURE

1. Triorganoindium(III) derivatives, R_3In:

R	Reference	R	Reference
CH_3	22	$C_2H_5-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-$	145
C_2H_5	47, 106		
C_3H_7	47	$C_2H_5-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-CH_2-$	145
n-,i-C_3H_7	45, 49		
n-,i-,sec-C_4H_9	45, 49		
C_5H_{11}	144	C_5H_5	139
C_6H_{13}	144	C_6H_5	146, 147
C_9H_{19}	47	C_6F_5 (ether)	57

2. 1:1 Addition compounds of trimethylindium

Ligand	Reference	Ligand	Reference
$N(CH_3)_3$	42	$S(CH_3)_2$	42
$P(CH_3)_3$	42	$N\text{-}Si(CH_3)_3$ ‖ $P(CH_3)_3$	148
$As(CH_3)_3$	42		
NH_3	42	$N\text{-}Si(CH_3)_3$ ‖ $P(C_2H_5)_3$	148
$O(C_2H_5)_2$	42		

3. Derivatives of dimethylindium(III), $(CH_3)_2In(B)$:

B		Reference	B		Reference
$O-CH_3$	trimer	42	$N(CH_3)_2$	dimer	42, 141
$S-CH_3$	dimer	42	$P(CH_3)_2$	polymer	14
$O-C(CH_3)_3$	dimer	149	$As(CH_3)_2$	polymer	14
$O-Si(CH_3)_3$	dimer	149	$P(C_2H_5)_2$	polymer	14
$O-Si(C_6H_5)_3$	dimer	149	$As(C_6H_5)_2$	dimer	13
CN	tetramer	41	$O_2P(CH_3)_2$	dimer	37
$C_5H_7O_2$		42	$S_2P(CH_3)_2$	dimer	37
NH_2	polymer	42			

4. Other organoindium derivatives

Compound		Reference
$(C_6H_5)_2InBr$		47, 146
$(C_6H_5)_2InI$		146
$C_6H_5InBr_2$		146
$C_6H_5InI_2$		146
$(C_6F_5)_2InBr$	dimer	57
di-α-naphthylindium bromide		47
C_5H_5In		138, 139
$CH_3In-P(C_6H_5)$	polymer	14
$CH_3In-As(CH_3)$	polymer	14
$CH_3In-As(C_6H_5)$	polymer	14

APPENDIX II

INFRARED SPECTRA OF ORGANOINDIUM COMPOUNDS

Spectra were recorded in nujol or halocarbon oil mulls. The abbreviations used are: s, strong; m, medium; w, weak; v, very; sh, shoulder; bd, broad.

Dimethylindium fluoride: 1180m, 1166w, 1030w bd, 980w, 720vs bd, 548s, 493m, 330s bd.

Dimethylindium chloride: 2995w, 2920w, 1178m, 1160w, 1015vw, 732vs bd, 558s, 488m.

Dimethylindium bromide: 1172w, 1158vw sh; 1030vw, 735vs bd, 554s, 486vw.

Dimethylindium iodide: 2995vw, 2915vw, 1165m, 1150vw sh, 975vw, 730vs bd, 548s, (480vw).

Dimethylindium chloride-pyridine: 2985vw, 2920vw, 1600s, 1489w, 1443s, 1240vw, 1212m, 1156sh, 1151m, 1060m, 1038m, 1008m, 762m, 748s, 720vs bd, 694s, 628s, 526s, 488m, 412m.

Dimethylindium iodide-pyridine: 2970w, 2905w, 1652vw, 1600m, 1482w, 1438m, 1350w, 1214w, 1148w bd, 1062m, 1041m, 1013m, 758sh, 720vs bd, 698 sh, 630s, 522s, 482m, 416m.

Dimethylindium chloride-triphenylphosphine oxide: 1590w, 1437s, 1335w, 1310w, 1186w, 1145s, 1118s, 1082s, 1068m, 1027w, 1019w, 997m, 970vw, 925vw, 845vw, 747m, 722vs, 690s, 615vw, 542s, 536s, 507w, 487w, 470w, 436vw, 395vw, 319w.

Dimethylindium chloride-triphenylarsine oxide: 1440s, 1340vw, 1310w, 1180vw, 1160vw, 1145vw, 1086m, 1065vw, 1022w, 997w, 878s, 860s, 745sh, 737s, 720m, 690s, 686sh, 610vw, 522m, 476sh, 469s, 462sh, 390w, 375w, 353m.

Dimethylindium chloride-x(tetrahydrofuran): 2975vs, 2875vs, 1456m bd, 1366w, 1340w, 1290vw, 1244vw, 1185w bd, 1160sh, 1067s, 1039vs, 914m, 878s, 720vs bd, 666m, 528s bd, 484m bd.

Dimethylindium iodide-triphenylphosphine: 1434m, 1180w, 1155w, 1095m, 1069vw, 1025w, 998w, 840vw, 742s, 724s, 708m, 692s, 512s, 495s, 478w, 432w.

Dimethylindium iodide-triphenylphosphine oxide (gum): 3170vw, 3150w, 3080s sh, 3055s, 2990s, 2915s, 2850sh, 2710vw, 2260w bd, 1975w bd, 1905w bd, 1825w bd, 1780w, 1680w, 1592s, 1578w sh, 1487s, 1438s, 1388w, 1337w, 1312m, 1280w sh, 1150vs bd, 1118vs, 1088s, 1070s, 1028s, 1000s, 980w sh, 925w, 848w, 745s, 723vs, 692vs, 615w, 540vs, 516m sh, 480m, 460m bd, 442m, 412m.

Bis(dimethylindium chloride)-triphenylphosphine: 1436m, 1310vw, 1178w, 1156w, 1096m, 1070vw, 1027w, 996w, 967vw, 847vw, 742s, 730s, 709s, 690s, 544m, 515s, 498s, 492s, 432w, 390vw.

Dimethylindium chloride-ammonia: 3325vs bd, 3250s, 3195s sh, 3150s, 2970s, 2920s, 1700w bd sh, 1600s bd, 1450vw, 1405w bd, 1265m sh, 1210vs bd, 1155m sh, 725vs bd, 528s, 486m.

Dimethylindium chloride-2-ammonia: 3320vs bd, 3250s, 3195s, 3150s, 1670w bd, 1600s bd, 1246w sh, 1202s bd, 1156w, 1148w, 1016vw, 717vs bd, 650m sh, 614w sh, 560vw, 530s, 520s, 480m, 340w.

Dimethylindium chloride-3-ammonia: 3390s, 3300vs bd, 3220s sh, 3170s sh, 2330vw, 2260w, 1840w bd, 1597vs bd, 1252s, 1146vs, 735vs sh, 712vs bd, 555m sh, 516s, 482w, 375w.

Dimethylindium iodide-ammonia: 3325vs bd, 3245s, 3185s, 3155s, 2980s, 2910s, 2270w, 1680m bd, 1598vs bd, 1770w bd, 1380vw, 1215vs bd, 1160w sh, 1015vw, 720vs bd, 590m bd, 524s bd, 482m, 320w bd.

Dimethylindium iodide-2-ammonia: 3250vs bd, 3210s sh, 3175s, 3125s, 1800w bd, 1598s, 1250s, 1244s, 1205w, 1152vw, 1015vw, 725vs bd, 686m sh, 630w, 610vw, 525s, 485m, 366m, 355m.

Dimethylindium iodide-3-ammonia: 3300vs bd, 3220s sh, 3180s, 3140s, 1750w bd, 1600s bd, 1228s, 1209w, 1170s, 1155s, 1130s, 720s bd, 690s sh, 662w sh, 606w, 530s bd, 482w, 450w sh, 338w.

Dimethylindium acetylacetonate: 1945w bd, 1595vs bd, 1560vs, 1515vs, 1248vs, 1215sh, 1203w, 1164w, 1158w, 1018s, 917s, 788m, 715s bd, 658m, 648sh, 550s, 540s, 486m, 410s.

Dimethylindium o-nitrophenoxide: 1603s, 1552s, 1485s, 1428s, 1350s, 1320s, 1252sh, 1226s, 1155s bd, 1081m, 1054w, 1039s, 882s, 824m, 775w, 740sh, 730vs bd, 690w, 655m, 592w, 568s, 550s, 523w, 497w, 448m, 399w.

Dimethylindium 8-hydroxyquinolinate: 1600w, 1575m, 1497m, 1425w, 1318s, 1274m, 1232w, 1172w, 1150w, 1102s, 1066w, 1032w, 976w, 903w, 860w, 822s, 802m, 790s, 745s, 730s, 705s bd, 640w, 610m, 572m, 530s, 508m, 498m, 483w, 392m.

"Dimethylindium 2-aminoethane sulphide": 3420w bd, 3310m bd, 1655m, 1575s bd, 1490s bd, 1335s bd, 1224w, 1185w, 1145w, 1050s bd, 1020m sh, 990s, 800w, 720sh bd, 700s bd, 620w, 600w, 505m, (460, 450, 430)s bd, 325w bd.

Dimethylindium chloride-phenanthroline: 1621w, 1590w, 1578w, 1515m, 1495w, 1430s, 1345w, 1224w, 1210vw, 1141m, 1100w, 1090w, 1018vw, 995w, 974w, 950w, 900w, 863m, 844s, 805w, 774m, 726s, 712s, 634m, 551w, 522s, 483m, 412m.

Dimethylindium chloride-bipyridine: 1601sh, 1598s, 1585m, 1575m, 1490w, 1437s, 1320m, 1314w, 1260w, 1244m, 1212w, 1174m, 1158m, 1149m, 1116w, 1100w, 1059m, 1040m, 1012s, 975w, 896w, 757s, 735s, 705s bd, 647m, 642s, 622m, 529s, 481m, 445vw, 407s, 345vw.
Chloroform solution: 3110w, 3070w, 2990vs, 2925m, 2875w sh, 1610s, 1600s, 1582m, 1572m, 1496m, 1482s, 1443vs, 1322s, 1174m, 1156s, 1118w, 1104m, 1075w, 1064m, 1044w, 1017s, 646s, 625m, 523s, 481m, 400m bd.

Dimethylindium iodide-bipyridine: 1602m, 1594m, 1570m bd, 1488w, 1435s, 1321w, 1313w, 1246m, 1215w, 1175m, 1155m, 1100w, 1058w, 1039w, 1012m, 974w, 897w, 760s, 725s bd, 647sh, 642m, 623m, 539s, 480vw, 445vw, 408m.
Chloroform solution: 525s, 478m, 405m, 395sh.

Dimethylindium chloride-ethylenediamine: 3355m, 3325s, 3305s, 3240vs bd, 3130vs, 1594s, 1331m, 1278m, 1152w sh, 1138m, 1103m, 1028s, 1018s, 1010s sh, 984m sh, 870vw, 720vs bd, 555w, 515s (bd), 481m (bd), 415w.
"solvate": 3355m, 3325m, 3295s, 3230s bd, 3155s, 3105s, 1603m, 1588s, 1335w, 1320w, 1285vw, 1276w, 1155m, 1105m, 1084w, 1048m, 1015s, 994s, 980s, 960m, 874w, 860w, 710vs bd, 650w sh, 582m bd, 516s, 504m sh, 484m, 420w, 355vw.

Dimethylindium iodide-ethylenediamine: 3320w, 3290m, 3220s bd, 3120s,

1590s, 1328m, 1280m, 1162m bd, 1105w, 1075vw, 1035s, 1017s, 1005s, 974s, 872w, 860w, 722vs bd, 565w, 520s bd, 491m bd, 407w, 373w. "Solvate", additional peaks at: 1615w, 900s.

Dimethyl(3,3,3-trifluoropropynyl)indium-etherate: 2980vs, 2950s, 2905s, 2155s, 1468w, 1446w, 1389m, 1242vs, 1211s, 1125vs bd, 1090m sh, 1052s, 1000w, 904m, 828w, 780m, 710s bd, 605w, 519s, 488m.

Dimethylindium-acetone complex [$(CH_3)_2In$-O-$C(CH_2)CH_3$?]: 2965s, 2920s, 2885m sh, 1691s, 1668s, 1618s bd, 1444s, 1378s, 1360s, 1276w, 1244m, 1220s, 1178s, 1166w sh, 1146m, 1112m, 1070m, 1030w, 1008w, 972m, 920s, 876m, 828m, 770m, 712s bd, 620w, 590w, 560m, 545m, 520s, 478m, 450m sh, 400w bd.

Dimethylindium methoxide: 2970s sh, 2920vs, 2890sh, 2810s, 2620w, 2290w, 2040w bd, 1645w, 1465m sh, 1448s, 1380w bd, 1262s, 1163s, 1090m sh, 1022vs bd, 800s bd, 705vs bd, 517s, 495s, 470vs.

Dimethylindium hydroxide (methylindium oxide probably present): 3420vs bd, 1166m, 1015m, 930s bd, 714s sh, 700vs bd, 524s, 470sh, 460sh, 400vs bd.

Methylindium oxide: 1182m, 1155w sh, 1015w, 970w, 720m sh, 677vs bd, 520s, 468s, 380vs bd.

Dimethylindium acetate: 2970w, 2905w, 1533s bd, 1446s bd, 1405m sh, 1162w, 1156w, 1050w bd, 1012m, 954m, 725s bd, 680s, 610m, 548s, 490m, 455w.

Dimethylindium trifluoroacetate: 3115w, 3000w, 2920w, 1805w bd, 1620vs bd, 1468m bd, 1200vs bd, 1175s, 1158s, 1016w, 870s, 796s, 750m sh, 734s, 598m, 564s, 518m, 497w, 430m bd.

Lithium tetramethylindate: 2060w, 1170vw, 1155vw, 1050vs, 1020w sh, 745vs bd, 510w sh, 430vs bd.

Tetraethylammonium dimethylindium dichloride: 1404s, 1308m, 1184s, 1148w, 1080m, 1030s, 1025s sh, 1004s, 798s, 715vs bd, 665w sh, 512s, 483m, 465w, 385vw.

Tetraphenylarsonium dimethylindium dichloride: 1442s, 1338w, 1314w, 1182w, 1161w, 1139w, 1078s, 1020w, 999m, 973w, 741s, 718m, 684s, 610vw, 512m, 489w, 470s, 453m, 358m, 332w.
Chloroform solution: 511m, 470s sh, 458vs, 340s.

Dimethylindium 1,1-bis(trifluoromethyl)ethoxide: 3000m, 2930m, 1655vw, 1462s, 1385s, 1304vs, 1264w sh, 1215vs bd, 1156vs bd, 1116s, 1080s, 1072s sh, 955s, 867s, 761s, 734vs bd, 706s, 701s, 650m, 620m, 540vs, 487m, 466m, 444m, 361w.

Methylindium dichloride: 1172m, 815m sh, 745vs bd, 720sh, 523m, 460vw, 280vs bd(?).

Methylindium dichloride-dipyridine: 1635w, 1600s, 1577w, 1485m, 1238w, 1215s, 1172vw, 1153w, 1068s, 1038s, 1007s, 950vw, 753s, 720m sh, 698vs, 625s, 512m, 420m, 295s(?).

Methylindium dichloride-bipyridine: 1610m, 1598s, 1577m, 1568m, 1490m, 1445s, 1315m, 1250m, 1220w, 1174m, 1152m, 1127vw, 1099vw, 1060m, 1042w, 1022s, 1015m sh, 968w, 890w, 770vs, 730s, 710s, 698s, 649m, 629m, (508w?), 496m, 413m.

Methylindium dichloride-terpyridine: 3510w bd, 1595s, 1580sh, 1575m, 1565m, 1480s, 1402w, 1317m, 1302w, 1275vw, 1262w, 1243m, 1197m, 1154m, 1090w, 1058w, 1028w, 1018s, 980vw, 938vw, 905vw, 837w, 784s, 737s, 722m, 661m, 648s, 640m, 522m, 510w sh, 448vw, 430w, 404w.

Dimethylthallium iodide: (1170vw, 1154vw), 800vs bd, 535w.
Dimethylthallium iodide in pyridine solution: 535m bd, 470w bd.

Dimethylthallium acetylacetonate: 2980w, 2915w, 1582vs bd, 1433vs bd, 1370vs bd, 1234m, 1004m, 905m, 785m bd sh, 770m, 648m, 540m, 524s, 494vw, 450vw, 404m, 390w sh.

Dimethylthallium acetate: (Perkin-Elmer 21) 3030vw, 2930vw, 1542vs bd, 1425vs bd, 1336w, 1233vw, 1168w, 1008m, 932m, 800s bd, 657vs, 615w, 550m, 493w, 456w, 415vw.

Bis[dimethylthallium] sulphate: 3020vw, 2930w, 1400m vbd, 1178w sh, 1060vs vbd, 810vs bd, 630s, 598s, 558s, 495vw bd, 410vw.

Dimethylthallium tetrafluoroborate: (Perkin-Elmer 21) 2950vw, 1675vw, 1595vw, 1415w bd, 1210m, 1110m sh, 1020vs vbd, 820m bd, 720w, 640vw, 560s, 540s bd.

Bis[dimethylthallium]carbonate (?): (Perkin-Elmer 137) 1640s, 1190w, 1100w sh, 1090s, 929m, 914m, 842m, 820sh, 797s bd, 722m, 707m, 688m, 613m, 598w, 545s bd, 538sh, 485w.

Dimethylthallium iodide-phenanthroline: 1620vw, 1588w, 1568vw, 1510w, 1428w, 1346w, 1135m, 1093m, 1077w, 1039vw, 1020vw, 958vw, 859m, 836s, 793s bd, 760m, 722s, 711s, 630m, 540s, 490w, 462w, 426vw, 410m, 390vw.

Dimethylthallium perchlorate-phenanthroline: (Perkin-Elmer 137) 1620w, 1590w, 1570w, 1510m, 1420m, 1405m, 1340m, 1300w, 1210w, 1200m, 1175m, 1140m, 1110s sh, 1090vs bd, 1065vs bd, 1040m sh, 930w, 860s, 855w, 840s bd, 804m bd, 762m, 725s, 716s, 632m sh, 622s bd, 550m, 495w, 467vw, 460vw, 415w bd.

APPENDIX III

PROTON MAGNETIC RESONANCE OBSERVATIONS FOR SELECTED ORGANOINDIUM DERIVATIVES

Spectra were recorded on a Varian Associates A-60 Spectrometer. Spectra were run at 37°C and signals were sharp lines, except where noted.

Compound	τ ($In-\underline{CH_3}$)	Solvent
CH_3InCl_2	9.75	ether
$(CH_3)_2InCl$	9.82	ether
	9.55 ± .02	deuterochloroform
	10.06	methanol
$(CH_3)_2InBr$	9.67	benzene
	9.36 ± .06	deuterochloroform
"$(CH_3)_2InBF_4$"	~10.0	methanol
$(CH_3)_2InCl$-bipyr	10.08	chloroform
$(CH_3)_2InI$-bipyr	9.79	deuterochloroform
CH_3InCl_2-bipyr	9.56	pyridine
$[(CH_3)_2InCl]_2$-$P(C_6H_5)_3$	9.52	nitrobenzene
	9.86	ether, -30°C
	9.85	nitromethane, -30°C
	10.14	methanol, -30°C
	~10.0	acetone, -30°C

Compound	τ	Solvent
$(CH_3)_2In-C\equiv C-CF_3-(ether)$	10.21	chloroform/freon 11
$(CH_3)_3In$	9.14	deuterochloroform
	10.05	cyclopentane (ref. 24)
	10.04	dichloromethane (ref. 24)
	10.19	benzene (ref. 24)
$Li^+ [In(CH_3)_4]^-$	10.78	ether
	10.63	ether, saturated solution
$(CH_3)_2In-O-C(CF_3)_2CH_3$ †	9.91, (8.48*)	deuterochloroform
	9.96, (8.52*)	freon 11, external TMS

† The ^{19}F nuclear magnetic resonance spectrum showed a single peak at 81 p.p.m. upfield from freon 11 ($CFCl_3$).

* This signal was split into three peaks (splitting about 2 c.p.s.), with shoulder peaks, and is assigned to the protons in $-C(CF_3)_2CH_3$. The ratio of the integrals of the peaks, 9.91 τ : 8.48 τ, is 2:1.

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